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The Journal of the Society of Dyers and Colourists

Volume 74 Number 4

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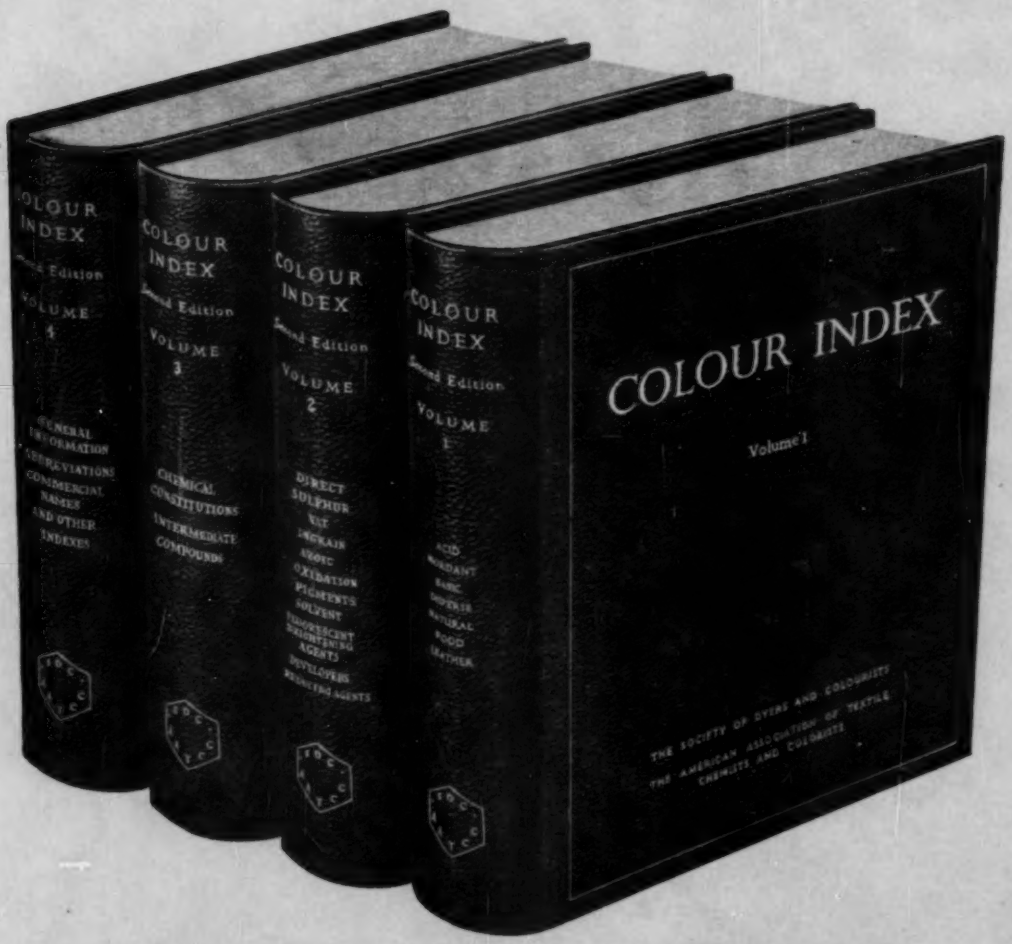

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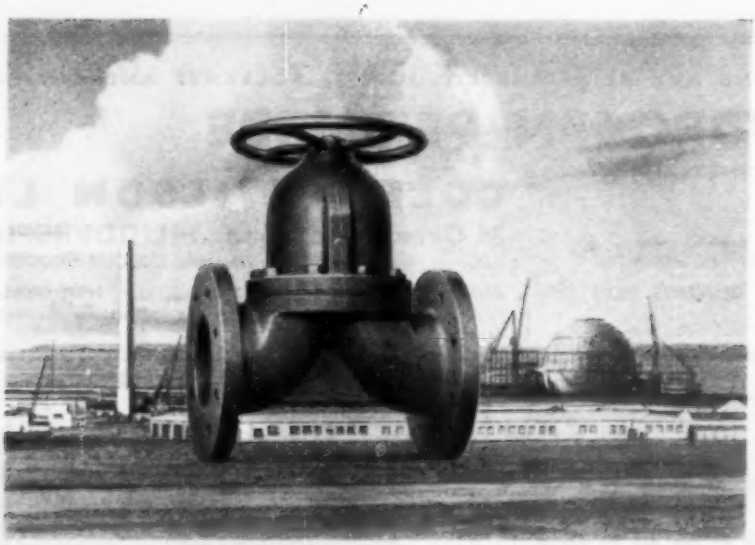

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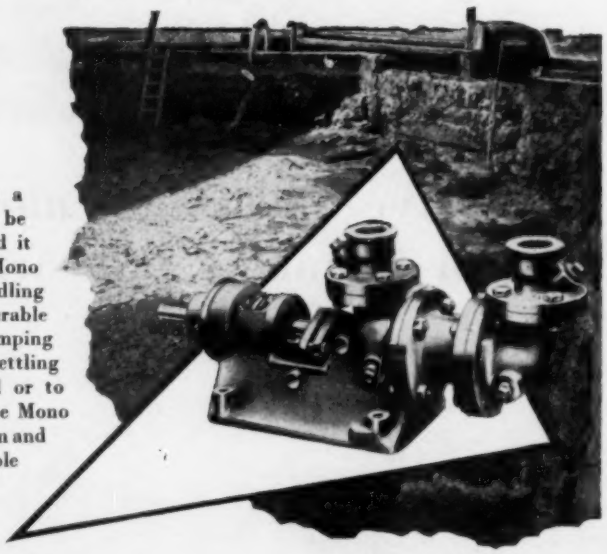

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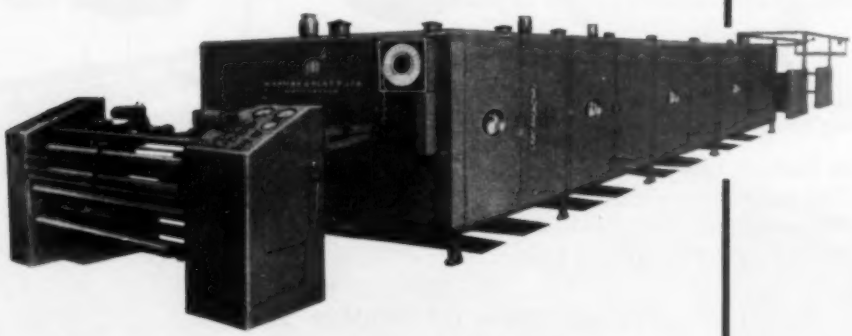

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Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–7 of the January 1958 and pages 285–290 of the July 1957 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Some Aspects of Bleaching with Hydrogen Peroxide and Peracetic Acid — *L. Chesner and G. C. Woodford*

The Dyeing of Fast-to-washing Colours on Wool Yarn — *J. F. Gaunt*

COMMUNICATIONS

Studies in the Transfer of Disperse Dyes to Cellulose Acetate during Steaming — *E. H. Daruwalla and V. R. Limaye*

Studies on Aminoanthraquinone Compounds
I— Absorption Spectra in Solution and in the Solid State
II— Photochemistry of Dyed Polymer Films
III— Photochemistry in the Solid State — *G. S. Egerton and A. G. Roach*

EXPLANATORY PAPER ON MODERN THEORY

Surface Activity, Solution, and Adsorption — *C. H. Giles*

FORTHCOMING MEETINGS OF THE SOCIETY

Friday, 25th April 1958

The Society's Annual General Meeting and Dinner. Central Hotel, **Glasgow C.1.**

Friday, 2nd May 1958

LONDON SECTION. Annual General Meeting and Dinner. Aldwych Brasserie, Aldwych, **London, W.C.2.** 6 p.m. for 6.30 p.m. (Mr. C. O. Clark will speak on the standards required for the A.S.D.C. examination.)

Friday, 24th October 1958

LONDON SECTION. Sixth London Lecture. *Colour in Art.* A. Lucas, Esq. Chief Restorer to the National Gallery. Waldorf Hotel, Aldwych, **London W.C.2.** 7 p.m.

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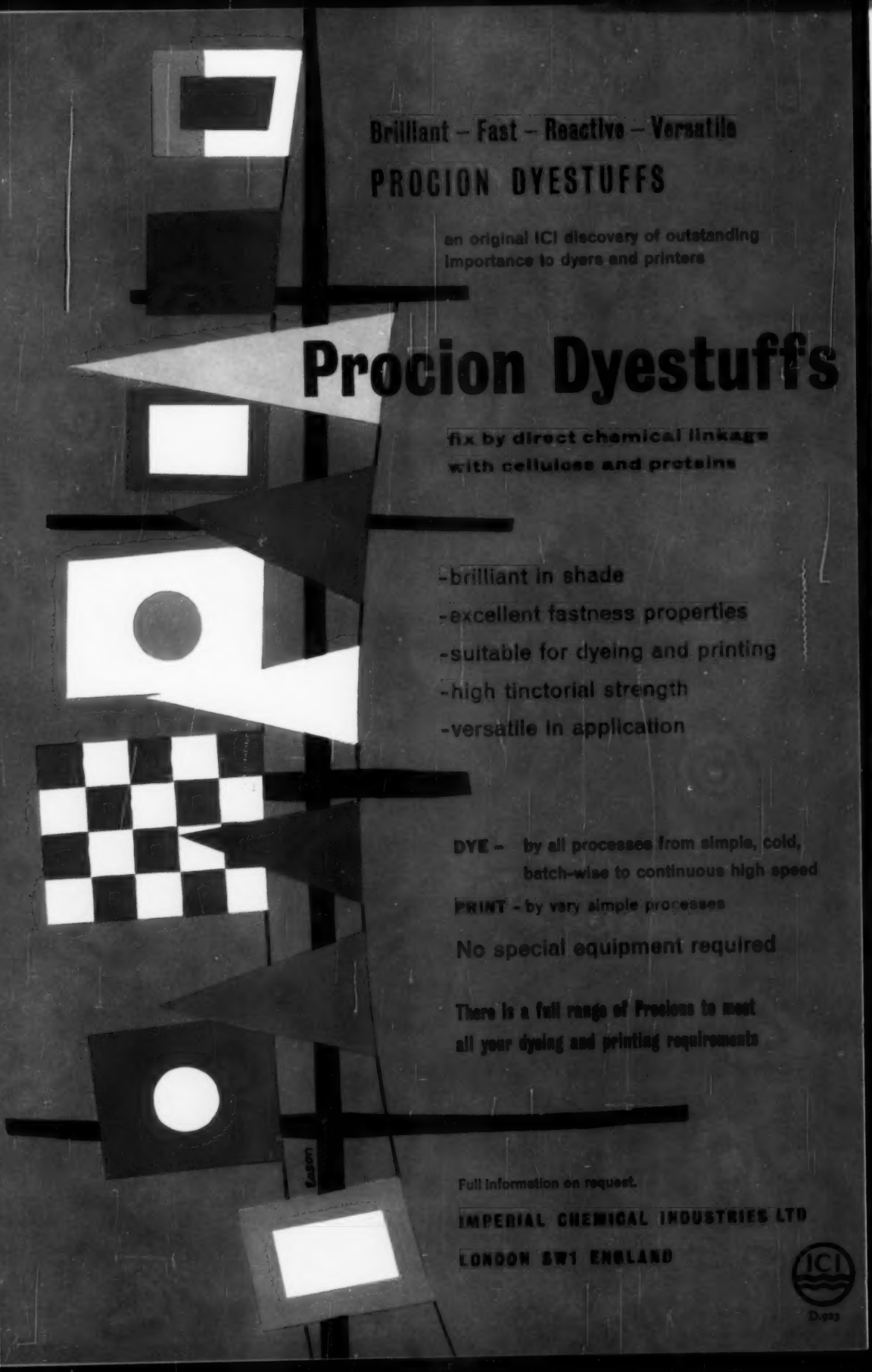
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Proceedings of the Society

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The Mode of Action of Non-ionic Levelling Agents

WERNER LUCK

Successful results in dyeing depend on a series of simultaneous equilibria. The formation of micelles by non-ionic levelling agents has been demonstrated spectroscopically and the micellar size determined. The equilibrium conditions in the formation of complexes between dyes and levelling-agent micelles have been studied. These conditions are intimately related to the equilibrium between dye and fibre. The latter equilibrium has been investigated with dyeings on polyamides. Study of the simultaneous equilibria dye–fibre and dye–levelling agent gives a clear picture of the nature of the retarding and levelling action of textile auxiliaries. The equilibrium between auxiliary and dye decreases the association of the latter. Results obtained in previous diffusion studies, however, have been interpreted as indicating increased association of dyes on addition of levelling agents. These results have been re-examined, and shown to be in accordance with the theories developed in the present paper.

Although it is often easy to obtain uniform dyeings with the aid of a suitable levelling agent, it is difficult to see precisely how the auxiliary produces this levelling. An attempt to explain the complicated effects of textile auxiliaries on a physical basis would appear at first sight to contradict the very nature of physical methods, which must be limited to idealised, simple processes.

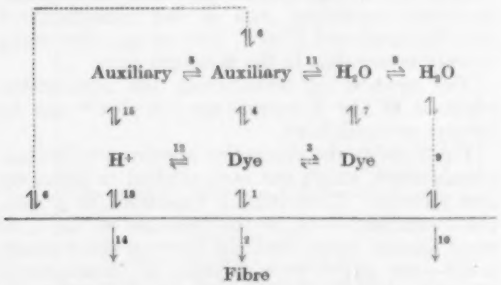


FIG. 1—Equilibria in Dyebath–Fibre System containing an Auxiliary Agent

Fig. 1 shows diagrammatically the interrelations of the large number of processes which in our experience play a part in producing a good dyeing. The most important magnitude is the affinity of the dye for the fibre (1). However, for many properties of a dyeing the depth of penetration of the dye into the fibre (2) may be as significant. Since with many dyeings thermodynamic equilibrium is not fully established, the kinetics of dyeing will be another important factor, which in turn is determined by processes (1)–(14).

We must remember that dyes associate (equilibrium 3), and this association may proceed as far as colloidal particles in dispersions of dyes. Apart from this, there exists an equilibrium between the dyes and the textile auxiliaries which have been added to the dyebath (4). The auxiliaries in turn are in a state of association equilibrium (5). In the case of some dyes we have been able to demonstrate that the attachment of water to the dyes (7) may be of importance. This in turn cannot be separated from the well known association of water molecules themselves (8). Further, the association of water is of importance for the interaction between water and the textile auxiliaries. Again, the molecules of the auxiliary agents can, owing to their surface activity, exert special effects on the surface of the fibre (6).

It is also known that the pH of the dye liquor can influence (12–15) all the processes mentioned thus far. Besides this there is the effect on all these processes of the presence of salt ions. For the sake of clarity this salt effect, which may be very important, has not been incorporated into Fig. 1.

The equilibria mentioned can now all be linked with one another, so that it is of no use studying them in isolation. Therefore the scheme in Fig. 1 shows very clearly that an exact elucidation of the dyeing process presents a very complicated problem. In our investigations we proceeded by studying an example of each individual process represented in Fig. 1. First we reported on studies on process (2), diffusion of dye in the interior of the fibre[1,2]. Even during these investigations it struck us that equilibrium (1) is not always established rapidly. In the case of natural fibres particularly, exact investigations of process (1) are difficult to carry out with sufficient accuracy. In the case of wool, for example, it is known that small differences in the chemical structure of the wool fibres result in unlevel dyeing[3]. Therefore, synthetic fibres are much more suitable for physicochemical investigations. For this reason polycaprolactam (6-nylon, poly-6-hexanolactam) fibres or films were chosen for the study of dye affinity.

During our experiments it struck us that the dye spectra of dyed polycaprolactam fibres suffer a shift in wavelength similar to that observed in solutions on addition of textile auxiliaries. A similar observation had already been reported by Derbyshire and Peters, who found spectral shifts accompanying formation of complexes between dyes in solution similar to those met in the spectra of dyed cellulose films [4]. Derbyshire and Peters, too, are of the opinion that complex formation between dyes is similar to the linkage of dye to fibre. On the basis of our investigations we believe that the formation of addition products between dyes and textile auxiliary agents represents a bonding similar to that occurring in the dyeing of polyamides. Therefore, in the course of our investigations we have studied most thoroughly the formation of these addition compounds and the molecular association of textile auxiliary agents. Spectroscopically the investigation of solutions is easier to carry out accurately than the study of films. For this reason, in the present paper we shall discuss, from our work on the physicochemical bases of dyeing, the interaction between dyes and textile auxiliary agents as well as the linking of this equilibrium with dye association and with the dye–fibre equilibrium (processes 1, 3–5, 15).

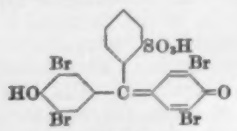
I— Dye-Auxiliary Equilibrium

Originally the action of the non-ionic levelling agents of the ethylene oxide type was ascribed to their properties as protective colloids [5, 6]. Valkó [7] discovered that non-ionic auxiliaries greatly reduce the rate of diffusion of dyes in solution. He explained these results by an increase in the particle size of the dyes, and assigned "aggregation numbers" to the dyes. His measurements are often even interpreted as showing that levelling agents act by causing aggregation of the dyes [7, 8]. This increased aggregation contradicts the idea that an increase of the particle size lowers levelling power [9–12]. On the other hand, the suggestion of Schöller, that there exist addition compounds between dyes and auxiliaries, has been discussed occasionally [13–18]. It therefore appeared to be urgently necessary that experiments be made which would clear up the problem.

1. DETERMINATION OF EQUILIBRIUM CONSTANTS

Preliminary experiments indicated the importance of concentration in the mode of action of non-ionic textile auxiliaries [19]. We tried, therefore, to find new methods which would actually prove the presence of addition complexes between dyes and auxiliaries.

We succeeded in working out a suitable spectroscopic method. As dye for these investigations we used Bromophenol Blue, which possesses the following chemical structure—



Bromophenol Blue

This dye was selected because, in view of its use as an indicator, it could be presumed that its dependence on pH (process 12, Fig. 1) would be of a simple character, which is confirmed by Fig. 2. In the acid pH range only one band, at 22900 cm.$^{-1}$ (437 mμ.), appears in the visible spectrum, and this absorption band may be ascribed to the undissociated form of the molecule. With increasing pH the intensity of this band decreases, and a new band appears at 16950 cm.$^{-1}$ (590·5 mμ.).

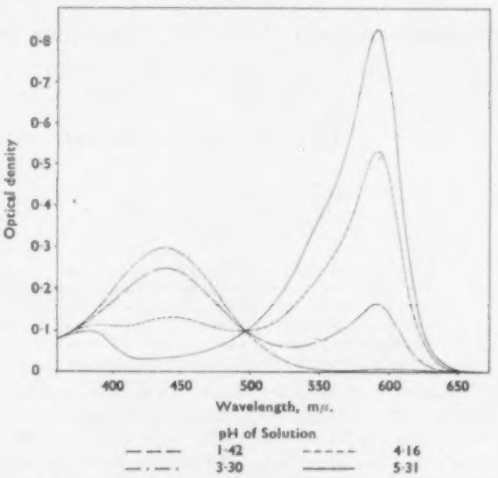


FIG. 2— Effect of pH on the Absorption Spectrum of Bromophenol Blue

Moreover, the accurate investigations made by Förster and König [20] on Eosin, which has a similar structure, confirmed that in our measurements with Bromophenol Blue we were using a dye which is truly monomeric in the dissolved state.

The method of determining the equilibrium constant of the dye–auxiliary complex [21] can be briefly outlined here.

Fig. 3 shows the absorption spectrum of Bromophenol Blue, which has been studied in detail by this method. If increasing quantities of a non-ionic auxiliary— e.g. in the example of Fig. 3 an oleyl alcohol which contains fourteen ethyleneoxy units— are added to a solution of Bromophenol Blue, the absorption band of the latter at 590·5 mμ. disappears, and a new band appears at 603 mμ., which we associate with the hypothetical dye–auxiliary addition complex. The various curves refer to different concentrations of this non-ionic product. The existence of a single point of intersection of all these curves (the isosbestic point) allows the explanation of these observations in terms of a simple equilibrium—

$$\underset{\text{Dye}}{D} + \underset{\text{Auxiliary agent}}{Hi} \rightleftharpoons \underset{\text{Addition complex}}{A} \qquad \text{(i)}$$

The band at 590·5 mμ. would then correspond to the free dye molecule and the band at 603 mμ. to the addition complex.

The equilibrium constant $\overline{K}$ of reaction (i) is defined by the equation—

$$\overline{K} = \frac{c_D \cdot c_{Hi}}{c_A} \qquad \text{(ii)}$$

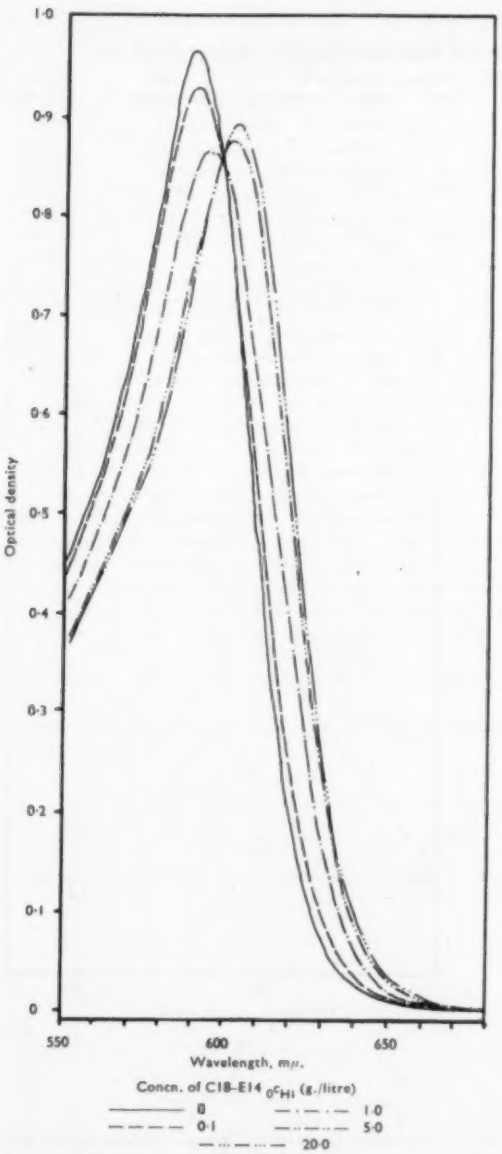


FIG. 3— Effect of Concentration of C18–E14 on the Absorption Spectrum of Bromophenol Blue (8·1 mg./litre; phosphate buffer of pH 7·97; 20°C.)

The concentration c_D of the dye and the concentration c_A of the addition product can readily be determined from the spectra. As shown in Fig. 4, we simply plot the optical density of the maximum of the band of the free dye at 590·5 mμ. against the concentration c_{HI} of the auxiliary agent. As a control the optical density at 603 mμ., i.e. the maximum of the band of the addition product, has been included in Fig. 4. Where the height of the new band has reached half its final value, c_D will be equal to half of the total concentration of dye in the solution. At the corresponding concentration of the auxiliary agent the other half of the total dye in the solution will be present in the form of the

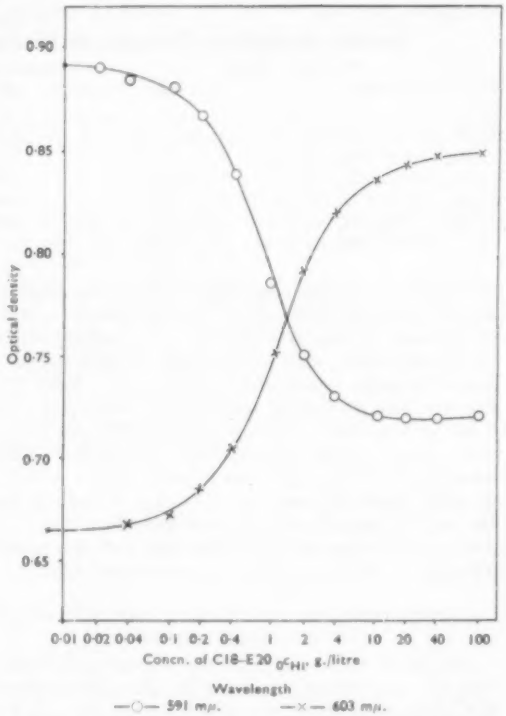


FIG. 4— Effect of Concentration of C18–E20 on Intensities of Absorption Bands in Bromophenol Blue Solutions (37·5 mg./litre; pH 7·97; 20°C.; K = 0·95)

addition complex. Thus, since we have $c_A = c_D$, this value of $_0c_{HI}$ is also the equilibrium constant (cf. equation ii).

Clearly, therefore, the equilibrium constant is equal to the concentration of auxiliary agent at which half of the dye is in the form of the addition complex.

Table I gives a series of equilibrium constants, determined by this method, for various polyethylene oxide derivatives of aliphatic alcohols. All constants relate to a pH of 7·97 (adjusted by means of a 0·067 M. phosphate buffer). ΔH is the heat of formation of the addition complexes.

The units in the equilibrium constant (ii) are molar for c_D and c_A, but the concentration of the auxiliary agent is expressed in grams per litre, since to begin with its molecular weight is not known. From an examination of e.g. the equilibrium constants at 20°C. for different auxiliaries, it is apparent that they are all of the same order of magnitude. If the addition product should be a compound of one dye molecule and one molecule of the auxiliary agent, then the equilibrium constant should be approximately proportional to the molecular weight of the auxiliary agent. However, it is plain that this is not the case, although the mean "molecular weight" has been varied by a factor of 6·5.

To explain this we have to consider whether it is a question merely of the total quantity of ether oxygen present in a given weight of auxiliary agent. This could certainly explain why only the quantity

TABLE I

Apparent Equilibrium Constants for Bromophenol Blue and Auxiliary Agents at pH 7·97

Auxiliary Agent Formula	Code	Apparent Equilibrium Constant $\overline{K}$ 10°c.	20°c.	30°c.	40°c.	60°c.	$-\Delta H$ (kcal./mole)	Mean Mol. Wt. ($\overline{M}$)
$C_{18}H_{35}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_{14}\cdot H$	C 18–E 14	—	0·8	—	1·04	—	—	890
$C_{18}H_{35}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_{25}\cdot H$	C 18–E 25	—	0·44	—	0·75	2·05	7·5	1370
$C_{18}H_{35}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_{80}\cdot H$	C 18–E 80	—	0·57	0·61	0·9	2·0	8	3800
$C_{16}H_{33}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_{26}\cdot H$	C 16–E 26	—	0·45	—	—	1·0	—	1390
$C_{12}H_{25}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_9\cdot H$	C 12–E 9	0·32	0·33	0·46	0·64	1·8	6–8	580
$H\cdot[CH_2\cdot CH_2\cdot O]_{100}\cdot H$	C 0–E 100	—	13	—	22	—	—	4400

of auxiliary agent, regardless of its molecular weight, determines its effect. Doubt is cast on this hypothesis by the fact that a pure polyethylene oxide derivative, with no aliphatic alcohol residue, has a far larger equilibrium constant (see Table I). Further, the spectra show that the nature of the bond in the case of polyglycols is different from that found with ethoxylated alcohols. The wavelength of the addition product shows a shift of only about 6·5 mμ. to 597 mμ. Moreover, in the case of polyglycols as additives there exist no real isosbestic points, and especially with the lower polyglycols we have rather a pure solvent effect.

2. ASSOCIATION OF AUXILIARIES; DETERMINATION OF MICELLAR WEIGHT

Now that we have found the above hypothesis, that the quantity of ether oxygen alone determines the addition of auxiliary agent to the dye, to be untenable, we have to consider how far interactions with other equilibria in Fig. 1 play a part. Thermodynamically, concentrations can be replaced by activities to take account of these effects, but for the practical man a closer investigation of the molecular picture would be of greater interest, in order to explain which kind of effects will produce these activities.

In the first instance, it will be necessary to examine our method of calculation more closely. For the concentration of auxiliary in equation (ii) we employed the concentration ${}_0c_{HI}$ before addition of dye. This must be corrected by subtracting from ${}_0c_{HI}$ the quantity of auxiliary linked to dye. This corrected concentration is designated c_{HI}. In Table I this correction has been neglected. This appeared permissible as a first approximation, as we used 7·5 mg. of dye per litre for all measurements referred to in Table I, and as we worked in the range of a few grams per litre in the case of the auxiliary agents. However, this assumption is permissible only if the molecules of the auxiliary agent do not show any strong association.

Thus it became necessary to determine the molecular size of the complexes of the auxiliaries, especially as micelle formation in solutions of non-ionic auxiliaries has already been discussed from time to time[22].

At first sight this determination of the molecular size of the association complexes appears to be a difficult task. According to previous work, the molecular weight of the micelles can be expected to be found in the intermediate range between the molecular weights which are determined by the normal ebullioscopic method on the one hand and those determined by macromolecular methods on the other.

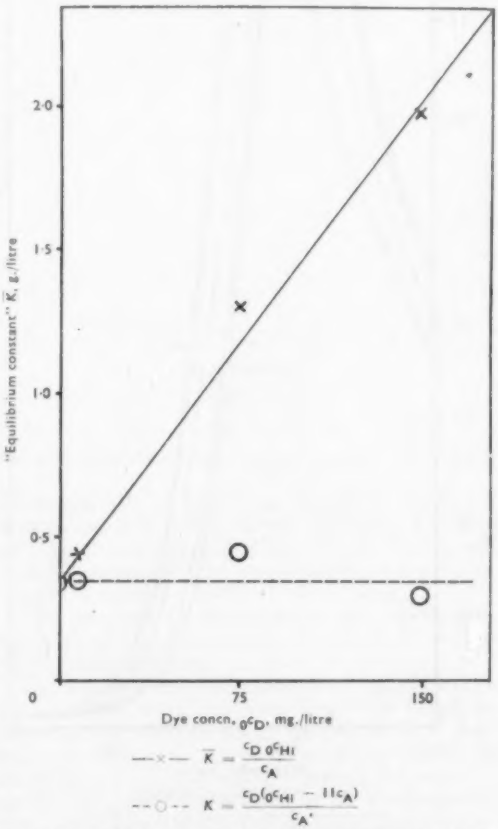


FIG. 5— Equilibrium Constants for Bromophenol Blue and C18–E25 at pH 7·97

However, a moment's thought showed that this problem, too, could be solved by means of our spectroscopic method. We merely varied the dye concentration and determined the equilibrium constant by the above approximate method. (The length of the absorption cell was varied so that the product of the concentration multiplied by the length of solution remained constant, i.e. so that the optical density remained the same.) Fig. 5 shows that for C 18–E 25 the equilibrium "constant" $\overline{K}$ in fact changes greatly with concentration of added dye ${}_0c_D$ (in contrast to ${}_0c_D$, the concentration of free dye, i.e. that which is not linked

to auxiliary, is represented by c_D). This variation may be expressed by the following equation—

$$\bar{K} = 0{\cdot}338 + 11{\cdot}29\ {}_0c_D \qquad \text{(iii)}$$

where ${}_0c_D$ is measured in grams per litre.

This linear relation can be explained quite simply by taking into account the removal of free auxiliary by formation of the complex, so that in calculating the equilibrium constants we have to subtract from the total concentration the amount bound in the addition complex. From equation (iii) it may be concluded that the quantity of auxiliary agent linked with the Bromophenol Blue by the addition reaction is very great. With 150 mg. of Bromophenol Blue per litre, 75 mg. of dye per litre will have been complexed at 50% addition. From our experiments it would follow that 1·677 g. of C 18–E 25 per litre has combined with the 75 mg. of dye and is no longer available for further addition. With 669 g. (1 mole) of dye 15,000 g. of C 18–E 25 would be associated. With a mean molecular weight of the latter of 1370 it follows that 11 molecules of the auxiliary are associated with 1 molecule of the dye. The broken line in Fig. 5 shows the equilibrium constants which would be obtained on the simple assumption that one molecule of dye is added to a micelle consisting of some eleven C 18–E 25 molecules. We thus obtain, with a scatter corresponding to the experimental error of our method, practically constant values for K.

The true equilibrium constant of our addition compound then becomes—

$$K = 0{\cdot}338 \text{ g./litre}$$

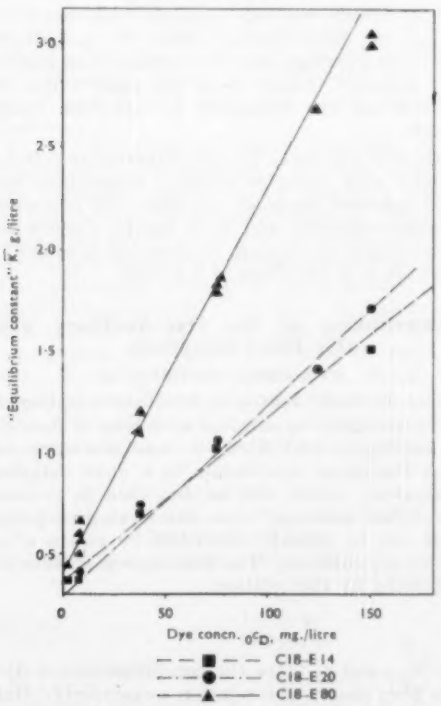


FIG. 6.—"Equilibrium Constants" for Different Levelling Agents and Bromophenol Blue

or, if we introduce an effective molecular weight of 15,000 (= 11 × 1,370) for the C 18–E 25—

$$K = 2{\cdot}25 \times 10^{-5} \text{ mole/litre}$$

In contrast to the apparent equilibrium constant $\bar{K}$ (equation ii), the true equilibrium constant K is defined by the equation—

$$K = \frac{c_D\, c_{HI}}{c_A} \qquad \text{(iia)}$$

so that for the concentration c_{HI} of auxiliary agent we now take only the quantity that is free, i.e. which is not linked to dye*.

Fig. 6 shows the apparent equilibrium constants to a first approximation as a function of the dye concentration for auxiliaries of different ethylene oxide contents. For all three cases we obtain straight lines. This variation of the apparent equilibrium constants with concentration is eliminated by assuming the effective molecular weights listed in Table II.

TABLE II

Molecular Weights and Equilibrium Constants of Different Sperm-oil Derivatives
$C_{18}H_{35}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_n\cdot H$

n	Effective Mol. Wt.	No. of Mol. per Micelle	K	K_{mol}
14	10,700	12	0·37	$3{\cdot}4 \times 10^{-4}$
20	14,000	10·2	0·27	$1{\cdot}9 \times 10^{-4}$
80	25,800	6·8	0·4	$1{\cdot}6 \times 10^{-4}$

Of course, the molecular weights thus obtained cannot be anything but mean values, since the ethylene oxide contents represent only mean values. Furthermore, our method determines only the quantity of auxiliary which belongs to a micelle, no account being taken of any water included in the complex. From further experiments the molecular weight seems to be purely a function of the ratio of the length of the aliphatic chain of the alcohol to the number of added ethylene oxide units. With these molecular weights we obtain the equilibrium constants in Table II. The equilibrium constants K_{mol} of the last column correspond to the hypothetical addition of one dye molecule to each micelle. They have been referred to one mole of the micelles.

This assumption of a 1 : 1 combination holds to a first approximation for dilute solutions. It requires further investigation to ascertain whether at higher concentrations of the dye, too, several molecules can be added to one micelle. At high concentrations certain deviations from the isosbestic point occur, which might indicate such a phenomenon. To a first approximation, however, especially for dilute solutions, our measurements can be explained quite well by the assumption of 1 : 1 complexes.

The term "micelle" here refers merely to the amount of auxiliary linked to one dye molecule. It is not possible from our spectroscopic method to say whether this unit quantity is identical with a single auxiliary micelle. Other methods, however, appear to indicate that this is the case.

* The concentration c_{HI} should theoretically be corrected by subtracting the concentration of auxiliary monomer. The correction is, however, very small in our graphical method of evaluation, and can therefore be neglected.

TABLE III

Apparent Equilibrium Constants for Bromophenol Blue at pH 1·42

Auxiliary	Apparent Equilibrium Constant $\bar{K}$				$-\Delta H$	$\bar{M}$
	10°C.	20°C.	30°C.	40°C.	(kcal./mole)	
C 18–E 25	0·05	0·06	—	0·085	3·5	1370
C 18–E 80	—	0·12	0·15	0·19	4·2	3800
C 12–E 9	—	0·1	0·12	—	—	580
C 0–E 100	—	—	—	100	—	4400

3. DEPENDENCE OF THE EQUILIBRIUM CONSTANTS ON pH

In the acid pH range, at pH 1·42, the indicator equilibrium of Bromophenol Blue is displaced nearly completely towards the side of the undissociated molecule (see Fig. 2). On investigating the absorption band (at 437 mμ.) of this "acid" form of the molecule on addition of ethylene oxide derivatives, a shift of the band with an isosbestic point is again observed. In this case, however, in contrast to the "alkaline" band, the shift occurs towards shorter wavelengths. Table III shows the apparent equilibrium constants determined for a concentration of the Bromophenol Blue of 10 mg./litre.

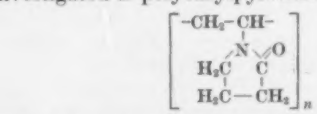
For ethylene oxide products these apparent equilibrium constants are considerably smaller than those which have been found for the alkaline form of the dye molecule. This means that in the acid range a smaller quantity of auxiliary is required to form a complex.

This difference in the mode of action of textile auxiliaries at different pH values can be shown by determining the reversible pH transition point. Addition of C 18–E 20 (2 g./litre) raises the transition point of Bromophenol Blue, determined optically from the spectrum, by a whole pH unit. This effect, known as the *protein error* of indicators, may be explained quantitatively from the measured equilibrium constants [19].

Micelle formation in the acid pH range is still under investigation.

4. THE ADDITION COMPLEXES OF POLYVINYLPYRROLIDONE

Another non-ionic product which we have investigated is polyvinylpyrrolidone—



with which, too, dissociated Bromophenol Blue forms addition complexes in alkaline solutions, the apparent equilibrium constants being given in Table IV. Again, a linear increase in apparent

TABLE IV

Apparent Equilibrium Constants for Bromophenol Blue and Polyvinylpyrrolidone

(Concn. of dye = 7·5 mg./litre; pH = 7·97)

Temperature, °c.	25	40	50
"Equilibrium constant" ...	0·85	1·2	1·45

equilibrium constant could be observed with increasing concentration of dye, which at 20°c. could be expressed by—

$$\bar{K} = 0{\cdot}83 + 4{\cdot}2\,{}_0c_D \qquad \text{(iv)}$$

From (iv) it would appear that one mole of dye is associated with some 5,600 g. of auxiliary. As the polyvinylpyrrolidone investigated has a mean molecular weight of 28,000, this result could be explained by assuming that several dye molecules add on to one molecule of polyvinylpyrrolidone. This idea of the addition of several dye molecules to one molecule of the auxiliary agent is consistent with the fact that with products of mean molecular weight 220,000 and 750,000 equilibrium constants of about 0·8 g./litre have been found, too. The mean molecular weight of polyvinylpyrrolidone has been measured by the physical methods of Hengstenberg and Schuch [23] and Scholtan [24].

At high concentrations of polyvinylpyrrolidone, of course, the isosbestic points become very ill defined, so that the figure of 5,600 represents only a very rough approximation. At a dye concentration of 150 mg./litre and high auxiliary concentrations there seems to be a second isosbestic point. This, however, could be explained by assuming that one dye molecule may be associated with two molecules of polyvinylpyrrolidone.

At all events, we can describe this complex addition of Bromophenol Blue to polyvinylpyrrolidone approximately by means of an equilibrium constant, which is of the same order of magnitude as the constants for ethylene oxide products.

In the acid pH region we find a different situation: here only very unstable addition compounds are formed between Bromophenol Blue and polymers of vinylpyrrolidone, and it is barely possible to determine any equilibrium constant, even roughly. At 25°c. it is of the order of 5 g./litre.

II— Interlinking of the Dye–Auxiliary and Dye–Fibre Equilibria

1. DYE–FIBRE EQUILIBRIUM

Before we could discuss in detail the coupling of the dye–auxiliary equilibrium with that of the dye between liquor and fibre, it was necessary to subject the latter equilibrium to a more detailed investigation, which will be described in a later paper. This indicated that the dyeing of polyamides can be formally described by means of a partition equilibrium. The distribution coefficient Q is defined by the relation—

$$Q = \frac{c_{D,f}}{c_{D,s}} \qquad \text{(v)}$$

where $c_{D,f}$ and $c_{D,s}$ are the concentrations of dye in the fibre and in the solution respectively. But we must remember that the value of Q varies with dye concentration, which is known to occur in

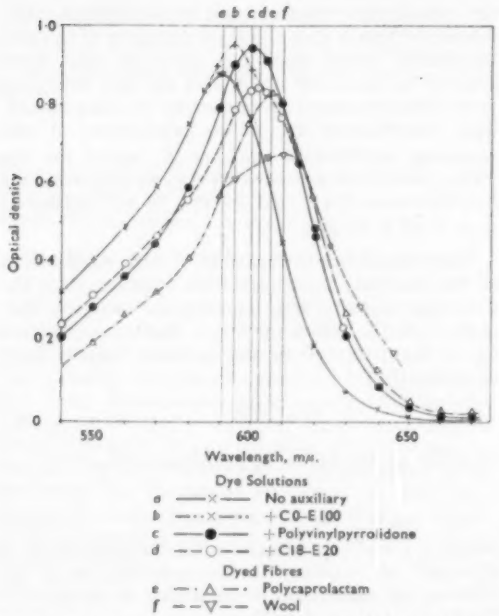


FIG. 7—Absorption Spectra of Bromophenol Blue in Solution and absorbed by Fibres (pH 7·97)

systems in which a reaction takes place during the distribution. The extent of the variation of Q with concentration depends on the pH.

Secondly, in the following discussion we shall assume that the mode of addition of dye to fibre is similar to that of dye to auxiliary agent. The affinity of the dye for the usual textile auxiliaries will be smaller than its affinity for the fibre. Fig. 7 and 8 will make this thesis somewhat clearer.

Fig. 7 shows the absorption spectrum of dissociated Bromophenol Blue in solution, alone and with different additions of auxiliary agents, and in (dyed) polycaprolactam film. A band could be observed in the same position when dyed polycaprolactam filaments were investigated by means of a home-made microspectrophotometer [1], which would take sections 10 μ. × 30 μ. By this method we succeeded in obtaining also spectra of wool fibres which had been dyed with Bromophenol Blue. Since it is not possible by means of a microtome to obtain good cross-sections of wool fibres, the spectra of which are completely free from skin effects, the spectrum of such a fine fibre

TABLE V

Location of the Maximum of the "Alkaline" Band of Bromophenol Blue

Addition or Substrate	Maximum of Band (mμ.)	Equilibrium Constant
None	590·7	—
C 0–E 100	594·4	13
Polyvinylpyrrolidone ...	600·5	0·8
C 18–E 20	602·5	0·3–0·4
Polycaprolactam film ...	606	—
Wool fibres	610	—

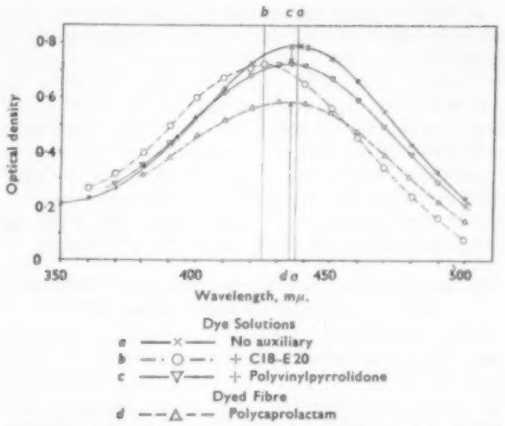


FIG. 8—Absorption Spectra of Bromophenol Blue in Solution and dyed on Fibre (pH 1·42)

cannot be obtained as sharp in all details as is possible with polycaprolactam fibres. The accuracy of the determination of the maximum is not affected by this phenomenon to so great an extent. In Table V are compared the maxima of the bands and the equilibrium constants measured.

Fig. 8 shows the absorption band of Bromophenol Blue in solutions of pH 1·42; for comparison a polycaprolactam fibre dyed at pH 1·42 has been included. The maximum of the latter coincides with that of microspectra of dyed polycaprolactam filaments. Table VI shows the relation between the absorption maxima and the equilibrium constants. In every case, the spectra refer to such large amounts of textile auxiliary that the equilibrium has been displaced towards the side of the addition complex.

TABLE VI

Location of the Maximum of the "Acid" Absorption Band of Bromophenol Blue

Addition or Substrate	Maximum of Band (mμ.)	Equilibrium Constant
None	437	—
Polyvinylpyrrolidone ...	434·5	5
C 18–E 20	424	0·06
Polycaprolactam film ...	434·5	—

Both these tables show a relation between the location of the band and the value of the equilibrium constant. If this rule can be confirmed in the future, this will result in a simple method of evaluating the efficiency of a textile auxiliary, and analytical applications are also conceivable.

According to these tables, in alkaline solutions the bond between dye and polyamide is stronger than that between dye and textile auxiliary agents. In acid solutions there exists merely a weak linkage with the polycaprolactam similar to that formed on adding polyvinylpyrrolidone, as compared with the linkage between the dye and the ethylene oxide derivatives.

A further example of the relation between dye affinity and shift of the absorption spectrum is given in a recent Russian paper [25], according to which increased substantivity of dyes is paralleled by an increased shift of the absorption maxima when the spectrum of dyed regenerated cellulose film is compared with that of the corresponding dye solution. Pineau, Fuson, and Josien[26] also have shown, by means of infrared studies, that the association equilibrium constant is proportional to the shift of the band maxima.

2. DESORPTION EXPERIMENTS— INFLUENCE OF THE AUXILIARY ON DYE MIGRATION

Our calculations have been carried out only on the basis of certain assumptions, and yet dyeing, as is shown in Fig. 1, is a very complicated process. It might be doubted, therefore, whether our spectroscopic method of determining the addition compounds between dye and textile auxiliary agent is of significance also in dyeing practice. However, the simple desorption experiments described below show that the order of magnitude of the equilibrium constants determined in the first part of this paper is of direct importance in dyeing.

In these experiments some wool was dyed at room temperature for a whole week in a citrate buffer solution of pH 1·2 containing Bromophenol Blue (1 g./litre). The wool sample was then immersed for a week in a blank buffer solution of pH 1·2 with and without an additive. The quantity of dye extracted by the solution was determined colorimetrically, the results being given in Table VII together with those for pH 8.

TABLE VII
Desorption of Dye from Wool

Addition	Dye extracted (mg./litre)	Equilibrium Constant K
pH = 1·2		
None	0·6	—
Polyvinylpyrrolidone (20 g./litre)	4	10
C 18–E 20 (20 g./litre) ...	53	0·06
pH = 8		
None	44	—
Polyvinylpyrrolidone (20 g./litre)	79	0·8
C 18–E 20 (20 g./litre) ...	78	0·28

The relation between the quantity of dye extracted and the order of magnitude of the equilibrium constant cannot be extended to a comparison of the results obtained under acid and alkaline conditions, because the wool is more deeply dyed under acid conditions, i.e. the affinity between dye and wool has to be taken into consideration in relation to both absorption and desorption of dye. Thus, as a result of these rough experiments, it may be concluded that the dye–auxiliary equilibria investigated in Part I are definitely linked with the equilibrium of the dye between fibre and dyebath.

In the last two lines of Table VII practically identical amounts of dye are extracted, although the equilibrium constants are quite different. The reason for this is that the same quantity of the two auxiliaries added does not represent the same number of auxiliary units, and the dye combines with different quantities of the two levelling agents. This experiment shows the usefulness of the apparent equilibrium constant $\overline{K}$, which for the 79 mg. of dye extracted with polyvinylpyrrolidone has the value 1·17, and for the 78 mg. extracted with C 18–E 20 $\overline{K} = 1{\cdot}21$.

Theoretically, combination of the equilibrium of the auxiliary agent addition complex with the dye–fibre distribution equilibrium may be calculated in the following way. The concentration c_D of the free dye in the solution follows from equation (iia)—

$$K = \frac{c_D c_{HI}}{c_A} \qquad \text{(iia)}$$

In addition, the following relations hold—

$$c_D + c_A = {}_0c_D \qquad \text{(vi)}$$

$$c_{HI} + mc_A = {}_0c_{HI} \qquad \text{(vii)}$$

where ${}_0c_D$ and ${}_0c_{HI}$ are the total concentrations of dye and of auxiliary in the solution; m is the number of molecules of auxiliary in a micelle. From (ii), (vi), and (vii)—

$$K = \frac{({}_0c_D - c_A)\,({}_0c_{HI} - mc_A)}{c_A} \qquad \text{(viii)}$$

If c_A is obtained from (viii) and substituted in (vi), then the following equation is obtained for the required concentration of free dye—

$$c_D = \frac{{}_0c_D}{2} - \frac{{}_0c_{HI}}{2m} - \frac{K}{2m} + \sqrt{\frac{1}{4}\left({}_0c_D + \frac{{}_0c_{HI}}{m} + \frac{K}{m}\right)^2 - \frac{{}_0c_D\,{}_0c_{HI}}{m}} \qquad \text{(ix)}$$

i.e.—

$$c_D = f({}_0c_D, {}_0c_{HI}, K, m) \qquad \text{(x)}$$

Thus, when a levelling agent is used, c_D is a function not only of ${}_0c_D$ but also of the total auxiliary concentration ${}_0c_{HI}$, the nature of the auxiliary (K), and its micellar size (m).

In the distribution equilibrium (v) the value for $c_{D,s}$ (dyebath) is analogous to that given by (ix), but with the modification that (vi) should now contain a term for the dye absorbed by the fibre—

$$c_{D,s} + c_A + c_{D,f} = {}_0c_D \qquad \text{(via)}$$

and hence (via) should be used to obtain the correct equation corresponding to (ix).

The results of the desorption experiments can be explained by means of equations (v) and (ix). If the dye is desorbed by means of a blank dyebath, then a certain concentration of dye c_D will be established in the liquor according to the distribution equilibrium (v). However, to maintain equilibrium (iia) this free dye will be removed into the addition complex with the auxiliary until equations (v) and (ix) are simultaneously satisfied. The total quantity of dye desorbed ${}_0c_D$ will thus be increased.

In the first instance, an exact evaluation of the desorption experiment is not worth while, as we

do not know whether, apart from (v), there exists a further distribution equilibrium between the addition complex with the auxiliary agent and the fibre—

$$Q_A = \frac{c_{D,f}}{c_A} \qquad \text{(xi)}$$

This can only be determined experimentally. For this purpose we carried out the fundamental experiments described in the following section.

3. RETARDING EFFECT OF DYE–AUXILIARY COMPLEXES

Polycaprolactam film was dyed at room temperature with a solution of Bromophenol Blue (37·5 mg./litre) in a phosphate buffer at pH 7·97 for 15 hr. The quantity of dye absorbed by the polyamide was then determined spectroscopically at the maximum of the absorption band, and Fig. 9 shows this quantity as a function of the concentration of C 18–E 20 in the bath. In the same figure is plotted the height of the band at 590·5 mμ. measured on the liquors prior to the dyeings, which gives directly the quantity c_D of free dye present in the solution.

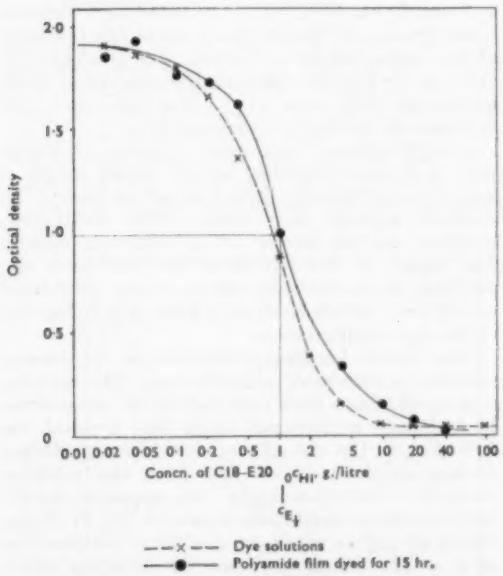


FIG. 9—Effect of Concentration of Levelling Agent on the Intensity of Light Absorption of Bromophenol Blue (37·5 mg./litre) in Solution and absorbed by Polyamide Film (phosphate buffer of pH 7·97)

The shape of the two curves is closely similar. At a concentration of the auxiliary agent of 1 g./litre, only half the quantity of dye has been absorbed by the polycaprolactam as compared with a dyeing without any additive. For this auxiliary a mean equilibrium constant of 0·95 g. per litre had been determined previously from the spectra of the solutions.

This important experiment can be explained on the hypothesis that dye molecules added on to the auxiliary agent have very little affinity for the polyamide as compared with free dye molecules, so that essentially the film will be dyed only by those dye molecules which are free in accordance with the dye–auxiliary equilibrium. Equilibrium (xi) can thus be neglected. The slight deviations between the curves in Fig. 9 can be explained in the main by a continuous production of free dye during the course of dyeing as well as by slight participation of dye associated with the auxiliary agent.

If to a first approximation dyeing is regarded as an equilibrium partition, then the retarding effect of non-ionic auxiliaries may be interpreted by means of the above model experiment. According to equation (ix) the concentration of free dye will be reduced by the auxiliary agent. Thus, the quantity of dye deposited on the surface of the fibre will be diminished according to the Nernst partition law (v).

4. CONCENTRATION-STABILISING EFFECT OF THE DYE–AUXILIARY COMPLEX

Levelling action depends upon the fact that, as dye is exhausted on to the fibre, fresh dye is released from the dye–auxiliary equilibrium according to equation (ix).

The results in Fig. 9 indicate the possibility that, in explaining levelling action, we need not be restricted to qualitative data. Knowing the dye–auxiliary equilibrium constants and the dye–fibre distribution coefficients, we are able to account for a model levelling experiment in which dye liquor is passed from left to right through a cylinder packed with fibres (Fig. 10).

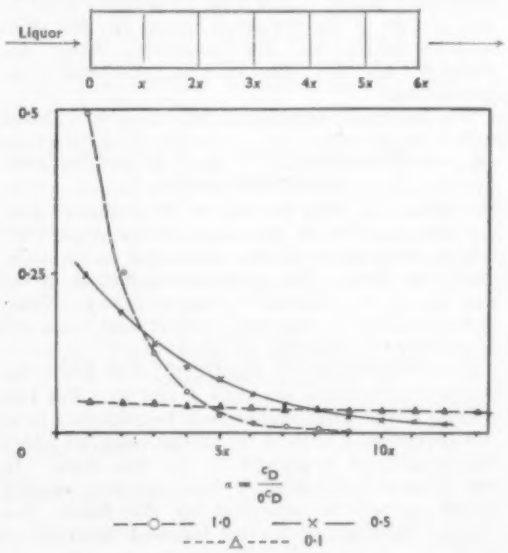


FIG. 10—Levelling Model

At the left-hand end of the cylinder (high concentration of dye) the fibres are strongly dyed. Suppose that the concentration of the dye is lowered by this first dyeing to such an extent that at the point x it is half its initial value $_0c_s$. With a true distribution coefficient, the concentration at a nx will be $_0c_s/n^2$. If we use one litre of liquor, the fibres in the compartments 0–x, x–$2x$, . . . absorb the following quantities of dye—

TABLE VIII

Effect of Auxiliary on Levelling

Position	Without Addition		With Auxiliary Agent $a = 0{\cdot}5$		
	$c_{D,s}$ (liquor)	$c_{D,f}$ (fibre)	$c_{D,s}$ (free)	$c_{D,s}$ (total in liquor)	$c_{D,f}$ (fibre)
0	1	0·5	0·5	1	0·25
$1x$	0·5	0·25	0·375	0·75	0·187
$2x$	0·25	0·125	0·2815	0·563	0·1407
$3x$	0·125	0·0625	0·211	0·422	0·1055
$4x$	0·0625	0·03125	0·158	0·3165	0·079
$5x$	0·03125	0·0156	0·1185	0·237	0·059
$6x$	0·0156	0·0078	0·089	0·178	0·0445
$7x$	0·0078	0·0039	0·067	0·134	0·0335
$8x$	0·0039	0·0019	0·05	0·101	0·025
$9x$	0·0019	0·0009	0·038	0·076	0·019
$10x$	0·0009	—	0·028	0·057	0·014
$11x$	—	—	0·0215	0·043	0·0107
$12x$	—		0·016	0·032	

$$\frac{{}_0c_s}{2},\ \frac{{}_0c_s}{4},\ \ldots\ \frac{{}_0c_s}{n^2}$$

Mathematically, the quantities of dye absorbed by the fibre in the individual compartments could be represented by the function—

$$c_f = {}_0c_f e^{-nx} \qquad \text{(xii)}$$

This equation is thus to be expected with partition equilibria. The theoretical curve is similar to the experimental exhaustion curves. Analogous considerations apply to the variation with time of the quantity of dye taken up at any given point, as soon as diffusion in the interior of the fibre is sufficiently rapid. Table VIII gives the concentration of dye in the liquor at points nx; the third column shows the dye quantities which are absorbed by the fibre in the individual compartments.

The imaginary experiment may now be repeated with a liquor containing a quantity of an auxiliary agent such that 50% of the dye is in the form of the dye–auxiliary complex and 50% is free ($a = 0{\cdot}5$). (In dyeing e.g. with 150 mg. of Bromophenol Blue per litre of a 0·67 M. phosphate buffer of pH 7·97, this would mean that 2·8 g. of C 18–E 25 has to be added per litre.) The partition coefficient of the free dye is not affected by the auxiliary. Thus, in our example, in the first compartment there will be absorbed by the fibre no more than $0{\cdot}5 \times 0{\cdot}5 = 0{\cdot}25$ of the total initial concentration of dye in the liquor (Table VIII, columns 4 and 6). For this reason, at the point x there will be present a total concentration of 0·75 of the initial value, of which half ($0{\cdot}375\ {}_0c_s$) is present in the free state. In the second compartment half of this amount ($0{\cdot}187\ {}_0c_s$) will be absorbed by the fibre. The further calculation can be followed from Table VIII.

From the last column of Table VIII an important feature of the levelling action of auxiliary agents can be understood. In the experiment carried out without auxiliary, only half the amount of dye is absorbed in each compartment compared with that absorbed in the preceding compartment. In the presence of the auxiliary, however, the corresponding ratio is 75%. As the eye is sensitive to light intensity, and according to Lambert's law this is a reciprocal exponential function of the concentration, these levelling effects from 50% difference to 75% difference may be considerable.

When the concentration of auxiliary is such that at any given time only 10% of the dye is present in a free state and 90% of it is linked to the auxiliary ($a = 0{\cdot}1$), the difference in the quantities of dye absorbed in succeeding compartments is very small, viz. 95%. Thus by selecting a suitable concentration of the auxiliary agent the levelness of the dyeing can be controlled. Fig. 10 shows the amount of dye absorbed in the individual compartments (0–x, x–$2x$, etc.). The value $a = 1{\cdot}0$ corresponds to the first experiment.

A high degree of levelness, however, is linked with a greater retarding effect, which means a longer time of dyeing. The two factors have to be weighed against each other. The auxiliaries, however, do not merely act as retarding agents. The supply of free dye from the micelles of the auxiliary is an additional effect, hardly considered up till now, which leads to a kind of stabilisation of the dye concentration.

The above imaginary experiment, of course, means a considerable simplification. The calculation should have been replaced by an integration. In addition, we have not taken into account the fact that, as the quantity of dye decreases during dyeing, auxiliary is set free from the addition complex. Correspondingly, the apparent equilibrium constant steadily decreases (cf. Fig. 6). Thus, during dyeing we pass from $a = 0{\cdot}5$ in the direction of $a = 0{\cdot}1$, which increases the levelling effect still further. The extent to which this occurs depends upon the molecular weight of the auxiliary.

Fig. 11 shows how the concentration of free dye depends on the concentration of C 18–E 80. These curves have been derived simply from the height of the band at 590·5 mμ.

Strictly speaking, the distribution coefficients themselves may vary with concentration.

For these reasons it is necessary to check our model by experiment. We exchanged the space coordinate of our imaginary experiment for the time coordinate. For a Bromophenol Blue concentration of 5 mg./litre in a phosphate buffer of pH 7·97 we have determined the half-dyeing time $t_{\frac{1}{2}}$, which was necessary for 50 g. of polycaprolactam film per litre to absorb half the total

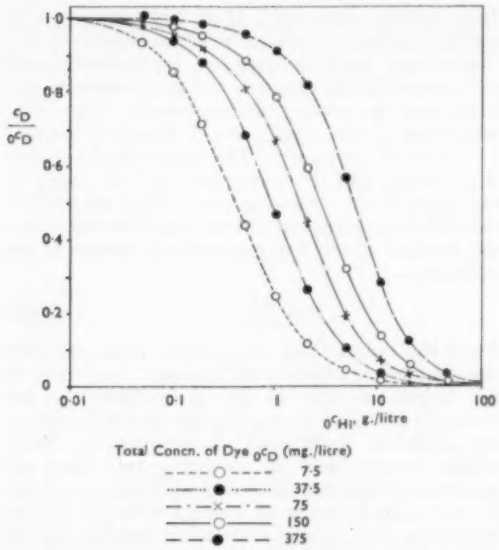


FIG. 11—Concentration of Free Bromophenol Blue in Bath as a Function of the Concentration of Auxiliary (C18–E80) and the Total Concentration of Dye in Solution (pH = 7·97) at 20°C.

concentration of dye, viz. 2·5 mg./litre. The dyed film was then removed and replaced by undyed polycaprolactam film, which was dyed for the same time. In order to avoid solvent losses, the volume of the dye liquor was cut down by 20% in this second experiment, and only 80% of the initial quantity of film was dyed. After a total time of $2t_{\frac{1}{2}}$ the film was replaced by undyed film again, and so on.

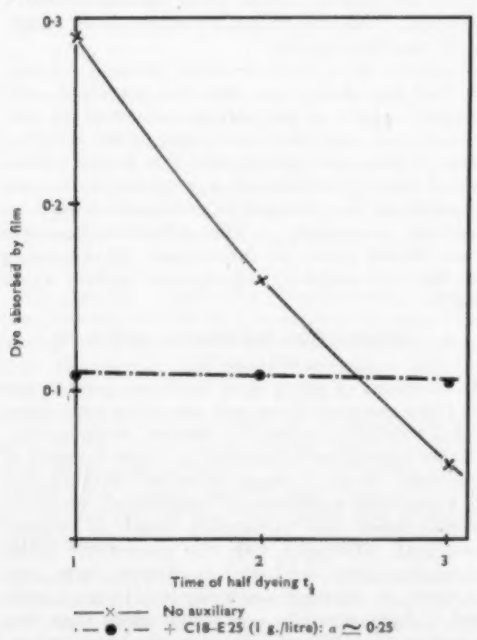


FIG. 12—Stabilisation of Concentration of Free Dye by Levelling Agent (Bromophenol Blue, total concentration in dyebath 5 mg./litre, pH 8; polyamide film dyed for 4 hr.)

Fig. 12 shows that in this manner, too, we obtain experimentally a curve corresponding to a partition equilibrium (unbroken line in Fig. 12).

If the experiment is repeated with different quantities of textile auxiliary added to the dye liquor, our imaginary experiment is confirmed in fact (broken line in Fig. 12).

On using increasing quantities of auxiliaries, each series of films is dyed more and more uniformly. The "stabilising effect" on the concentration can, of course, be derived from equation (ix).

5. SIGNIFICANCE OF DYE–AUXILIARY COMPLEXES IN LEVELLING

Summarising our results, we can distinguish five effects of levelling agents—

(*a*) As the dyebath concentration tends to decrease as a result of absorption on the fibre, free dye is continually supplied from the dye–auxiliary complex to maintain the equilibrium.

An example of this stabilising action is provided by package dyeing: as in our model experiment with the cylinder of fibres, the concentration of the dyebath will decrease when the dye solution is pumped in. When it enters the interior of the material, the lower concentration may lead to unlevel dyeing. If an auxiliary is added, however, the rate of decrease of the concentration will be diminished.

(*b*) The auxiliaries act as retarding agents.

(*c*) The ability of the dye to migrate will be increased, which leads to better levelling.

(*d*) The auxiliary also cleans the fibre, improves the wettability, and assists level dyeing in this way.

(*e*) The auxiliary aids in dispersing the dye (cf. Part III, below).

III—Effect of Dye–Auxiliary Equilibria on Dye Association

1. LOWERING OF THE ASSOCIATION OF THE DYE

In the past the view has been expressed that addition of non-ionic textile auxiliaries greatly increases the particle size of dyes, as in Table IX, published by Valkó [7].

TABLE IX

Effect of Auxiliary on Dye Association according to Valkó [7]

Dye	Peregal O (IG) (%)	Association No.
Chicago Blue 6B (IG)	0	4
	0·1	22
Indanthren Brilliant Green FFB (C.I. Vat Green 1)	0	3
	0·06	420
Palatine Fast Blue GGN (C.I. Acid Blue 158)	0	1·2
	0·1	10
Orange II (C.I. Acid Orange 7)	0	1·7
	0·1	5

Such an increase in the association of the dye is difficult to reconcile with our ideas. Any association is proportional to the concentration of the monomers. However, dye–auxiliary addition compounds reduce the concentration of free dye, as

may be seen from equation (x), so that the extent of association must be lowered.

TABLE X

Dispersing Effect and Equilibrium Constant
(grams of dispersing agent per litre)

Auxiliary	Dispersing Effect: Azoic Dye	Dispersing Effect: Indanthren Brilliant Green	Equilibrium Constant: Bromophenol Blue
C 18–E 14	—	3·0	0·8
C 18–E 20	1·6	1·1	0·44
C 18–E 80	1·4	0·8	0·57
C 0–E 100	—	No effect	13
Polyvinylpyrrolidone	2·35	1·9	0·8

On the other hand, observations on the dispersing action of textile auxiliaries, summarised under the name *solubilisation*, agree with our views [27–29]. Schwen and Rackemann [30] even went so far as to suggest determination of dispersing power as a standard method of test for textile auxiliaries. Table X shows that there exists a certain correlation between dispersing power (expressed as the weight of dispersing agent per litre necessary to dissolve 1 g. of dye per litre) and the equilibrium constants obtained by our method. On Valkó's hypothesis the Schwen–Rackemann method for assessing levelling effect would have no significance.

This discrepancy can be cleared up by the spectroscopic method. Fig. 13 shows that with increasing concentration of Bromophenol Blue a new band appears at 560 mμ., while the original band decreases in intensity. According to the investigations of Förster and König [24] on Eosin, which has a similar structure, the original band is produced by the monomeric form of the dye, whereas the new band is produced by the associated form of the molecule. If a large quantity of textile auxiliary is added to these solutions, the "associated" band becomes very much weaker, and an increase in the strength of the monomeric dye band can be clearly demonstrated. The concentration of dye aggregates is therefore lowered by the textile auxiliary. The discrepancy between these results and those obtained by Valkó may be explained in the following way: Valkó determined the diffusion coefficient D and from this calculated the radius r of the dye molecules by means of the equation—

$$D = \frac{kT}{6\pi\eta r} \qquad \text{(xiii)}$$

From the radius thus determined, Valkó specified the association numbers of the dye. According to our hypothesis that at any given time one dye molecule is linked to one micelle of the auxiliary, the diffusion coefficients determined by Valkó might be explained by assuming that they are governed by the radius of this addition compound. In that case, however, it would not be permissible to deduce from r any association number for the dye.

When Valkó states that Palatine Fast Blue in Peregal solutions consists of aggregates of ten dye molecules, this would still mean a particle of ten molecules on our views. However, the aggregate whose size has been determined by the diffusion method would now consist of one dye molecule and about ten molecules of the auxiliary.

In an internal report which has not been published, Valkó also determined the rate of diffusion of our product C 18–E 20, and found that the molecules were aggregated with a molecular weight of 15,000. This value shows excellent agreement with the value which we have determined spectroscopically.

Moreover, in a footnote Valkó himself pointed out that his association numbers represent only apparent values, as the particles observed by him consisted not only of dye but also of the levelling agent. From our experiments this is the crucial point. The hypothesis of aggregates containing dye alone in the presence of auxiliaries should be discarded completely. The diffusion measurements would then be interpreted by assuming that the dye–auxiliary aggregates migrate more slowly.

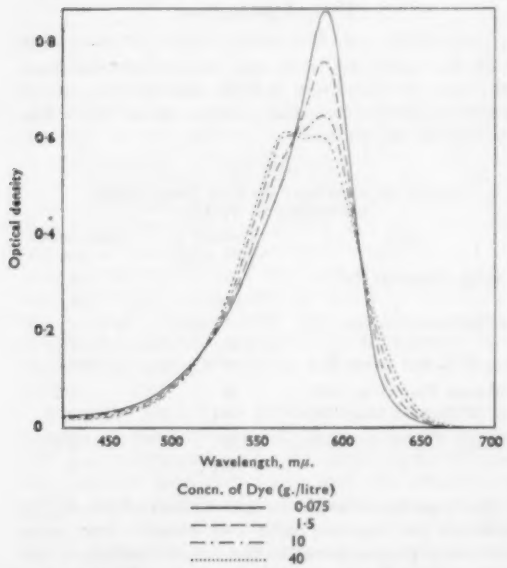


FIG. 13— Effect of Concentration on Absorption Spectrum of Bromophenol Blue, showing Association of Dye (0·33 M. phosphate buffer, pH 7·97; 20°C.)

2. AGGREGATION-INHIBITING EFFECT OF AUXILIARIES

In solutions of many dyes there are present not only the monomeric form and associates containing a small number of molecules (dimers, trimers, etc.) but also aggregates containing a larger number of molecules. As an example, Scheibe [31] investigated the absorption spectrum of pinacyanol chloride. He associated the absorption band of longest wavelength (600 mμ.) with the monomeric form, the intermediate band with a dimeric form, and the band of shortest wavelength (515 mμ.) with some higher aggregate containing more than five molecules. In this case also a marked strengthening of the monomeric band could be observed on adding C 18–E 25 (see Fig. 14).

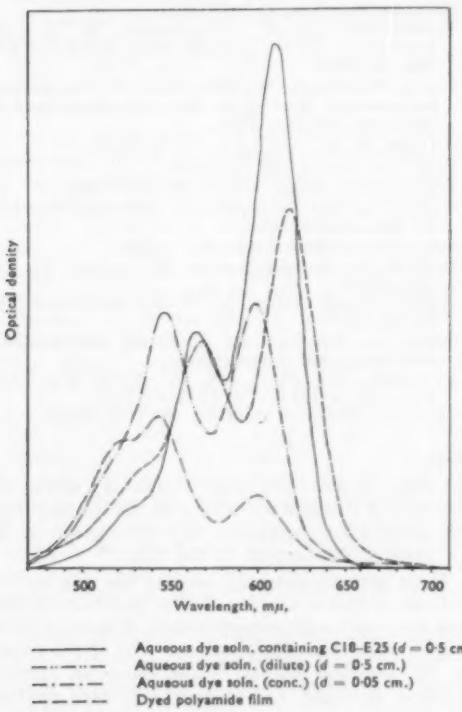


FIG. 14—Absorption Spectra of Pinacyanol Chloride (*d* = length of absorption cell)

This effect of auxiliaries may be shown in a different manner: if pinacyanol solutions are passed through a filter consisting of paper, sintered glass, or a plug of wool fibres, a completely colourless filtrate is obtained. Scheibe has established that polymerisation of pinacyanol chloride occurs at surfaces. Evidently, this polymerisation occurs on our filters, too. When we repeat these filter experiments with an addition of C 18–E 25, the dye passes through the filters without any decrease in the depth of colour: polymerisation on the filters has been prevented.

This model experiment demonstrates another characteristic of levelling agents: with dyes which tend to undergo colloidal flocculation, this tendency may be reduced by the dye–auxiliary addition complexes.

Fig. 14 shows a displacement of absorption band on addition of auxiliaries similar to that observed with Bromophenol Blue. These shifts can also be shown with completely different groups of dyes, so that we believe that our results are of general significance.

Fig. 14 shows clearly how the monomer content increases on addition of auxiliaries. Here, again, the band displacement may be observed in dyed polyamide films. This displacement corresponds to that observed on adding auxiliary agents in solution, but is more intense in the dyed films.

Experimental

All spectra mentioned in this paper were obtained with the self-recording Cary spectrophotometer, type 14. The absorption cells were kept at a constant temperature by means of a thermostat.

The products C 18–E 14, C 18–E 20, and C 18–E 80 were purified by the method of E. Plötz (private communication). By this means some fractionation of the molecular weights, as well as a purification from salts and polyglycols, may be obtained.

All investigations were carried out with 0·067 M. buffer solutions, and the equilibrium constants given here refer only to these ionic strengths. On adding salt or increasing the molar concentration of buffer, a change in the equilibrium constants as well as in the molecular weights will occur. These complex phenomena will be discussed in a subsequent paper.

It should be emphasised that our spectroscopic method is only an approximate method, worked out with the aim of clarifying the complicated processes to some extent. For this purpose we had to introduce certain simplifications. In particular, the ethylene oxide contents are only mean values. Further, at higher concentrations the 1 : 1 addition reaction is likely to be replaced by more complicated processes. We believe, however, that by means of the approximation described here we have made some advance.

* * *

The author would like to express his thanks to the management of the Badische Anilin- und Soda-Fabrik and in particular to Professor W. Reppe and Dr. G. Schwen (Chief Colourist) for the opportunity of carrying out these investigations and for permission to publish this paper, and for useful suggestions; and to his colleagues—Fräulein B. Hänsel, E. Teschauer, and K. Qualen, and Herren W. Ditter and G. Zapf—for their assistance in the experimental work.

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Discussion

Mr. H. R. HADFIELD: Dr. Luck has demonstrated, most elegantly, the effect of auxiliary products in promoting level dyeings by the mechanism of a restraining effect. I am, however, not certain from the paper how improved migration is obtained.

Dr. LUCK: In my view our results, expressed in the form of equilibrium constants, also show increased migration. In the descriptive explanation the only reason why we have dealt with the retarding effect more thoroughly is that it is easier, of course, to prevent an unlevel dyeing than to level it subsequently. The desorption experiments with wool were intended to show the direct relation between the equilibrium constants obtained and the migration of the dye. The levelling of regions which have been too deeply dyed consists of two separate processes— firstly the removal of the excess dye and secondly the absorption of this dye on the insufficiently dyed regions. The first process is accelerated by the auxiliary–dye addition compounds, dye passing into solution at the fibre surface in accordance with the partition equilibrium. The auxiliary–dye addition compounds now absorb this dissolved dye, lower the concentration of free dye in the liquor, and in this way effect an increased total concentration of dye in the liquor, which is analogous to the restraining effect. Table XI gives the results of an experiment of this type with polycaprolactam films which had been dyed with Bromophenol Blue at pH 1·42. The dyed films were then treated, in the presence of undyed films, with solutions containing different concentrations of auxiliary at 50°C. for 4 hr. Table XI shows the quantity of dye still remaining on the initially dyed film after 4 hr., expressed as a percentage of the dye originally taken up by the film.

TABLE XI

Desorption Experiment with Polycaprolactam Films

C 18–E 20 (g./litre)	Dye on Dyed Film (%)
0	63·9
0·1	56·7
0·2	53·5
0·5	49
1	39·6
2	31·8
20	24·6

These percentages hold only for the dye concentrations of this example. As the partition coefficients may vary with concentration, it is not possible to generalise from these values. One of the papers by Mr. Hadfield himself [32] also shows an example of how levelling can depend on the dyebath concentration.

The second process, reabsorption of the dissolved dye, on the other hand, may be retarded. It is thus possible that there is an optimum concentration of auxiliary agent for the levelling of unlevel dyeings. It follows that the correct addition of auxiliaries must be based on experience, or else the makers' recipes should be followed.

Mr. R. J. HANNAY: Following the question put by Mr. Hadfield regarding the apparent paradox in the claims that first a restraining or retarding effect in the speed of dyeing is involved in this technique, and secondly that possibly an increased rate of migration of the dye within the fibre could take place or that migration in unevenly dyed material is rendered more easy, may not the explanation be that, just as the retarding effect on rate of dyeing can be partly ascribed to the prevention of aggregation of the dye molecules in solution, so the dye molecules are also prevented from, or retarded in rate of, aggregating, even when transferred from the solution to the fibre, thus enabling the dye to migrate more freely within the fibre?

Dr. LUCK: Certainly the levelling of unlevel dyeings must be considered in the light of the general theory of interlinked reactions, as they are collected together in Fig. 1. The lowering of association in the solution by auxiliary agents certainly also assists levelling, but this is not the whole story. Accelerated desorption can be demonstrated even at concentrations at which no association can occur. The auxiliary agents will have less effect on association in the interior of the fibre in the case of polycaprolactam.

Actually, a retarding effect and a more rapid migration are only apparently contradictory. They can arise from the same equilibria.

Furthermore, such surface effects as wetting, removal of fat, etc. must be considered.

Mr. HANNAY: In the paper the author has investigated the effect of varying chain length in the end-groups of the auxiliary and also the effect of varying the number of ethylene oxide groups. Has any investigation been made of the effect of altering the type of end-chain from a straight chain to a highly branched chain or *vice versa*? Such a change can often make even greater changes in the characteristics of an auxiliary product than increasing or decreasing the number of carbon atoms in the chain.

Dr. LUCK: Products with branched aliphatic groups have not been investigated so far. As a working hypothesis we regard the auxiliary agent units as containing the aliphatic groups, linked together by dispersion forces at the centre, while the polyethylene oxide groups project into the aqueous phase like the tentacles of an octopus. It is quite conceivable that the products mentioned by Mr. Hannay would behave differently in our experiments, owing to the different spatial configuration of molecules containing branched chains.

Dr. W. FURNESS: It appears that there are some analogies between the action of non-ionic levelling agents in dyeing and the action of maximum-suppressors in polarography. In polarographic studies it is usually desirable to ensure that the diffusion of ions and molecules down concentration gradients towards an electrode surface is controlled in accordance with Fick's laws. For that purpose, even though electrical migration of charged ions may have been eliminated by the presence of an indifferent electrolyte, it is often necessary to introduce a maximum-suppressor. The various maximum-suppressors undoubtedly function in several different ways, but their precise modes of action are not fully understood. However, as a result of their ability to become adsorbed upon, and to modify the isoelectric point of, the electrode surface, or as a result of their ability to form micelles in solution or to prevent the association of electro-oxidisable or electro-reducible substances in the vicinity of the electrode, maximum-suppressors are helpful in practical work in providing steady conditions for diffusion. It seems possible that progress in the investigation of polarographic maxima would assist understanding of the action of levelling agents in dyeing, and *vice versa*. It would be interesting to determine whether levelling agents for dyes are generally useful as polarographic maximum-suppressors, and whether those dyes which are notoriously difficult to apply level give rise to extreme polarographic maxima on electrolytic reduction.

Dr. LUCK: The substances investigated by us are all suitable for use as maximum-suppressors. As an example, Table XII shows the height of the maximum in solutions of copper sulphate with different additions of C 18–E 20.

TABLE XII

C 18–E 20 (g./litre)	Maximum (mm.)
0	35
0·001	15
0·002	6
0·003	3
0·004	0·3
0·005	0

Polyvinylpyrrolidone and polyglycols have been investigated as maximum-suppressors by Wiele and Gerlich [33]. On addition of C 18–E 20, the maximum vanishes approximately in the concentration region in which the surface tension–concentration curve flattens out. This suggests that the maximum results from changes in surface tension. The interfacial tension between mercury and solutions of electrolytes also shows a maximum as a function of the applied voltage [34]. According to Lippmann [35] the electrical double layer is affected by movement of the mercury surface, in such a way that, in accordance with le Chatelier's principle, the change in curvature of the mercury drop resulting from the changed interfacial tension opposes the movement of the mercury surface. This suggests that the drop will vibrate, and maxima may be produced. I would therefore think that the action of maximum-suppressors is due to their surface tension and to their effect on the electrical double layer (and rather less to processes in the solution). The electrical double layer, of course, plays a part in dyeing, too, although its precise effect has not yet been determined. Glenz [36] has recently studied the effect of interfacial potentials in dyeing. The two phenomena are certainly related. It is not clear whether it would be easy to relate the complex phenomena directly with one another. It is certainly true that the electrical double layer at non-metallic interfaces has been very little investigated up till now.

Dyeing Hydrophobic Fibres in Solutions of Solvents

M. K. GOKHALE, L. PETERS, and C. B. STEVENS

Data are presented concerning the rate of dyeing of cellulose triacetate loose staple fibre with 3% Duranol Red X3B 300 (C.I. Disperse Red 11, C.I. 62015) from aqueous solutions of *n*-butanol or benzyl alcohol.

In water saturated with *n*-butanol, more than 85% exhaustion is reached after 1 hr. at 80°C., 30 min. at 60°C., or 1 hr. at 40°C. After 30 min. in water saturated with benzyl alcohol, 68% of the dye present is fixed on the fibre at 40°C., 78% at 60°C., and 80% at 80°C. In general, with either solvent, the highest amount of dye fixation is obtained at about 60°C. At higher temperatures less solvent is needed and the time of dyeing can be reduced.

A method for dyeing Tricel (BrC) or Terylene (ICI) in fabric form is suggested.

Following the discovery that aliphatic alcohols assist the dyeing of wool and silk at temperatures lower than is usually considered possible [1], it was thought interesting to examine their effect on the dyeing of man-made fibres.

Polyamides are so similar chemically to proteins that no great surprise was felt when nylon and polyurethan materials were successfully coloured by similar methods. But theory suggested that the sphere of application must be wider. Hydrophobic fibres, in general, ought to have affinity for the sparingly soluble alcohols used, and dyes for such fibres ought to be readily soluble in such solvents.

Cellulose itself would not be classified as hydrophobic, but the highly acetylated forms, especially the triacetate, seem to offer likely prospects. Terylene has long been dyed by the carrier technique, but usually organic solvents are chosen which swell the material and, at present, the use of dispersions of insoluble assistants is regarded as superior to that of water-soluble substances [2]. The number of substances which have been applied is truly enormous, and it would be futile to claim to have discovered something not already tried. Nevertheless, studies in great detail are not readily available, and this justifies presenting for publication work of this kind. The behaviour of Acrilan and Orlon has been investigated, but the results, though promising, are too meagre yet to be included here. Here, therefore, data are presented mainly concerning the rate of dyeing of cellulose triacetate (Tricel) with one dye, 1:4-diamino-2-methoxyanthraquinone (Duranol Red X3B) from aqueous solutions of *n*-butyl alcohol and of benzyl alcohol.

MATERIALS

The cellulose triacetate (Tricel) was provided by British Celanese Ltd., and was in the form of loose fibre (cut to 2½ in. staple), semi-dull, 3 denier, originally tinted faint purple. Before use, it was scoured twice in 0·1% Lissapol C (ICI) at 80°C., then thoroughly washed twice in hot water and twice in cold water, and hydroextracted before being left to condition in a room maintained at 65% R.H. and 20°C.

The dye used was Duranol Red X3B 300 powder fine (ICI) (C.I. Disperse Red 11, C.I. 62015). Its absorption spectrum was compared with that of a pure specimen of 1:4-diamino-2-methoxyanthraquinone, kindly supplied by Mr. C. L. Bird, of the Department of Colour Chemistry and Dyeing of Leeds University. The spectra seemed the same, apparently with no other coloured component present in the commercial product.

n-Butanol and benzyl alcohol (both of Laboratory Reagent (BDH) quality) were the solvents employed as dyeing assistants.

METHOD

Rate-of-dyeing experiments were usually carried out with a Lister spool dyeing machine.

The conditioned triacetate (60 g.) was packed in the machine and immersed in 1450 ml. of water or water saturated at 20°C. with *n*-butanol or benzyl alcohol, the liquor having been brought to the required experimental temperature beforehand and maintained within ± 0·5°C. The liquor was then circulated through the material for not less than 15 min. to ensure complete wetting-out, before addition of 50 ml. of a solution containing 1·8 g. of Duranol Red X3B 300, i.e. 9% of standard dye on the weight of the conditioned triacetate at a liquor ratio of 25:1. Evaporation losses in the experiments of long duration were minimised by a lid specially made to fit the central shaft of the machine.

The concentration of dye in solution was estimated by diluting convenient aliquots in 20% acetone and measuring the optical absorption with a Spekker absorptiometer fitted with a Hilger green filter No. 5.

The dye fixed on the fibre was defined as that retained by the dyed material after being scoured once in a 1% solution of Teepol (Shell) at room temperature and then rinsed thoroughly in cold water 5 or 6 times. Very little colour was thus removed, and the dye remaining was extracted in a Soxhlet apparatus with pure trichloroethylene until the material was completely white again. Such trichloroethylene extracts were diluted to known volumes and then compared with similar standard solutions of dye.

The optical absorption of the solutions of benzyl alcohol was determined with a Unicam SP 500 ultraviolet spectrophotometer.

N-BUTANOL

Table I shows the rate of dyeing of cellulose triacetate staple fibre at 40°, 60°, and 80°C. in presence and absence of *n*-butanol (78 g./litre). Equilibrium is reached after only 2 hr. at 40°C. in water saturated with the alcohol, whereas even 240 hr. is not sufficient in the absence of the alcohol.

TABLE I

Effect of *n*-Butanol (77 g./litre) on Rate of Dyeing

Time of Dyeing (hr.)	Dye fixed on Fibre in Absence of Solvent (%)	In Water saturated with *n*-Butanol	
		Dye fixed on Fibre (%)	Dyebath Exhaustion (%)
	At 80°C.		
0·25	23·1	83·5	80·0
0·5	31·1	85·1	83·3
1·0	42·5	86·5	87·1
2·0	53·0	86·5	90·2
12	82·5	—	—
24	—	89·4	—
48	85·1	—	—
	At 60°C.		
0·25	8·1	82·1	84·5
0·5	12·5	84·8	87·5
1·0	18·0	86·8	90·2
2·0	20·5	89·1	92·7
4·0	—	89·4	—
7·0	32·5	—	—
11·25	—	94·1	—
24·5	42·1	—	—
240	72·2	—	—
	At 40°C.		
0·25	—	66·2	74·5
0·5	—	73·9	80·7
1·0	—	77·5	85·0
2·0	—	82·1	89·6
4·0	—	80·8	—
24	14·4	—	—
120	27·8	—	—
144	—	81·6*	—
152·5	32·5*	—	—
240	43·1*	—	—

* Experiments in which samples were merely immersed in stoppered flasks in a thermostat and shaken occasionally.

The dye fixed on the fibre, defined as that remaining after the thorough scouring described above, is expressed as a percentage of the total dye originally present.

From the dye remaining in solution in the dyebath at various times, the exhaustions in the last column were obtained. The equilibrium exhaustion values of the dyebath appear to be 91·0, 93·4, and 91·6% at 40°, 60°, and 80°C. respectively. When the logarithms of how far the solution is from equilibrium are plotted against time, straight lines are obtained (Fig. 1). These, extrapolated to zero time, give the following estimates of the "equilibrium strike" in presence of alcohol, i.e. of the combination which would occur if the dye did not diffuse into the fibre—71% at 40°C., 83% at 60°C., and 78% at 80°C.

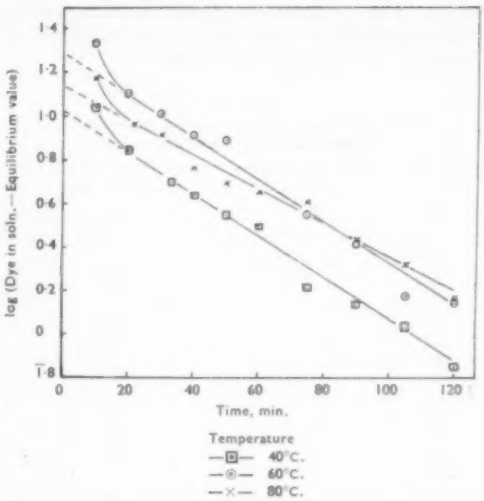

FIG. 1—Plot of Exponential Approach of Dyebath Concentration to Equilibrium

The rate of "dyeing" (i.e. the slope of these straight lines), as distinct from the rate of "strike", is hardly affected by temperature, the values being 10, 9·4, and 8·2 per 1000 min. at 40°, 60°, and 80°C. respectively. There is thus little or no heat of activation for diffusion into the fibres, if that is what is measured by the slow change in concentration. Estimates of the diffusion coefficient are of the order of $4{\cdot}5 \times 10^{-11}$ cm.²/sec.

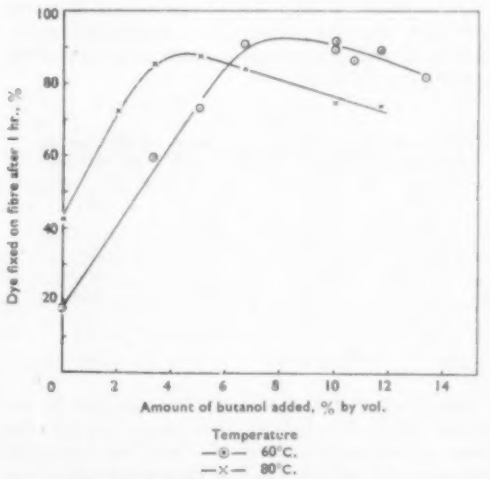

FIG. 2—Effect of Different Concentrations of *n*-Butanol on Dye Exhaustion after 1 hr.

Taking the exhaustion after one hour as a standard, the effect of varying the amount of butanol was then studied. The results plotted in Fig. 2 show that, at 60°C., the maximum exhaustion is attained when sufficient alcohol is added to saturate the solution completely. When still more alcohol is added, the exhaustion does not fall until the material becomes saturated, but the decrease is slight even when there is a visible excess of

butanol. This contrasts markedly with the effect of water-insoluble carriers, such as naphthalene or diphenyl in the dyeing of Terylene [3].

TABLE II

Effect of Temperature on the Aqueous Solubility of Alcohols

Temperature (°C.)	Benzyl Alcohol (% by wt.)	*n*-Butyl Alcohol (% by wt.)
10	—	8·9
20	3·93	7·8
25	3·98	—
30	4·07	7·1
35	4·105	—
40	4·14	6·6
45	4·196	—
50	4·194	6·5
55	4·365	—
60	—	6·5
70	—	6·7
80	—	6·9
90	—	7·7
100	—	9·2

Raising the temperature to 80°C. only reduces the maximum dye fixation from 93% at 80 g. of butanol per litre to 88% at 40 g./litre. But this latter is not the equilibrium value: the lower optimum concentration of alcohol is no longer the saturated solution (69 g./litre at 80°C.), because the higher temperature has speeded up the process, so that after 1 hr. the system is now nearer to equilibrium.

BENZYL ALCOHOL

This solvent is less soluble in water than is *n*-butanol, but its solubility is somewhat more affected by changes in temperature, as is shown by the data in Table II.

TABLE III

Effect of Temperature on Rate of Dyeing in presence of Benzyl Alcohol (3·6% by volume)

Time (hr.)	Percentage of Total Dye fixed on Fibre 40°C.	60°C.	80°C.
0·25	61·9	80·2	—
0·50	67·6	77·8	79·5
1·0	65·1	79·5	82·5
2·0	65·3	80·2	75·8
4·0	66·25	—	—
8·0	—	79·5	—
24	67·9	—	79·5

Benzyl alcohol is denser than water and is less volatile than butanol, so that there are smaller losses by evaporation. It also has less odour, is more pleasant-smelling, and is thus more suitable as a possible practical assistant in dyeing. Its effect on the rate of dye fixation on cellulose triacetate is more dramatic, too, in that equilibrium is reached more rapidly than with butanol, as can be seen by comparing the data of Table III with those of Table I.

Taking the degree of dye fixation after 1 hr. as a standard, the effect of varying the temperature is shown in Fig. 3.

Varying the amount of this alcohol affects the amount of dye fixed on the fibre after 1 hr. (Fig. 4).

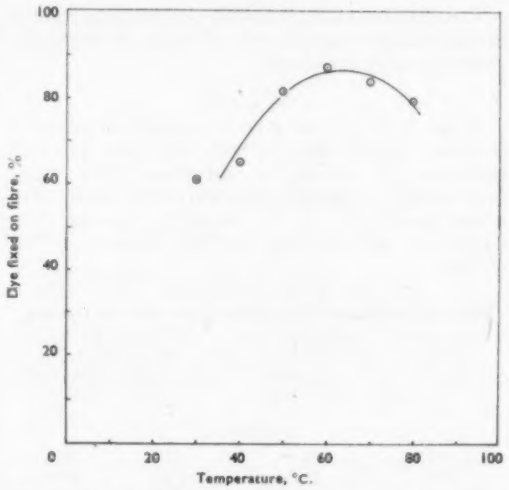

FIG. 3— Effect of Temperature on Dye Absorption from Water saturated with Benzyl Alcohol

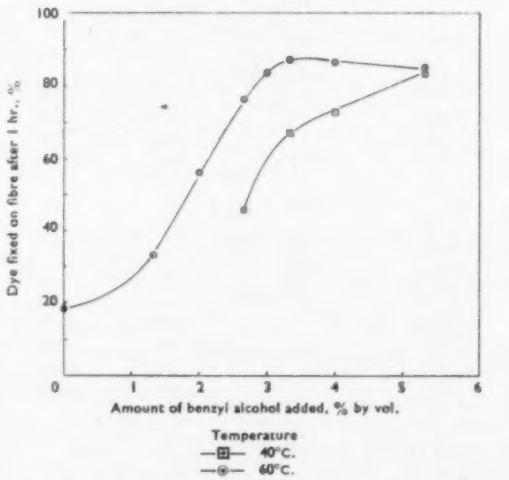

FIG. 4— Effect of Concentration of Benzyl Alcohol on Dye Uptake

The maximum of 87% fixation at 60°C. is in close agreement with that for *n*-butanol, showing that the solvent does not alter the nature of the dyeing process, but merely speeds up the approach to what would be the same ultimate equilibrium.

Aqueous solutions of benzyl alcohol, fortunately, have a characteristic peak of optical absorption in the ultraviolet at 257·2 mμ. (Fig. 5), and this provides a method for estimating its concentration. After allowing samples of the triacetate sufficient time (2 days) to come to equilibrium with solutions containing different quantities of benzyl alcohol, the amounts of alcohol absorbed by the material were evaluated from the changes in concentration. The results thus obtained are presented in Fig. 6, the data being remarkably like those for water-absorption isotherms.

From Fig. 4 and 6 we can estimate the dye fixation corresponding to any given amount of

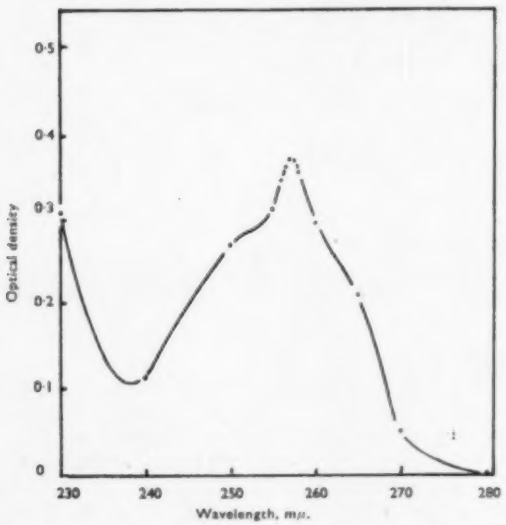

FIG. 5— Optical Absorption Spectrum of Aqueous Benzyl Alcohol (0·21 g./litre)

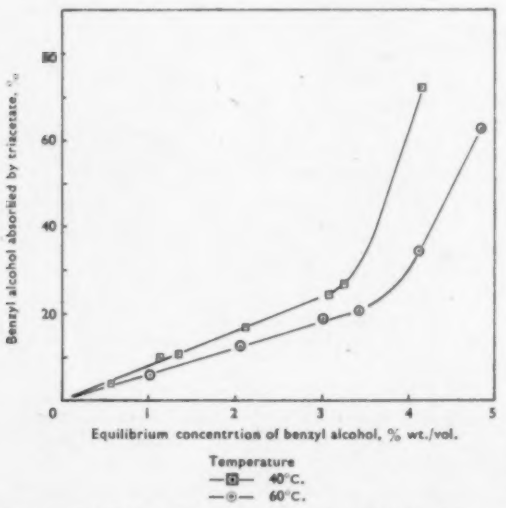

FIG. 6— Equilibrium Absorption of Benzyl Alcohol by Cellulose Triacetate at 40° and 60°C.

alcohol absorbed. It seems that, when 15% benzyl alcohol (on weight of material) is absorbed, a dyebath exhaustion of as much as 83% can be obtained in 1 hr. at 60°C. This is a good value for the heavy dyeing obtained, but, to avoid loss of the excess alcohol, the bath would then have to be used again with the addition of 17% benzyl alcohol (on the weight of the material) to replenish the bath. The additional 2% is estimated to make up for the imbibed solution taken out of the bath. For dyeing Tricel–wool mixtures with diethyl phthalate as carrier in a 40:1 liquor, a 0·5% solution is recommended [4], and this corresponds to 20% of carrier on the weight of material. No data are at present available on the amount of carrier unabsorbed in such dyebaths, but it seems probable that very little may be left, and the whole of this 20% must be regarded as lost, in which case the use of benzyl alcohol might be as satisfactory as that of diethyl phthalate as far as cost is concerned.

On the other hand, the preservation of exhaust dye liquors presents difficulties, and it seems preferable to avoid this problem by an entirely different approach. The speed of combination and fixation in presence of benzyl alcohol seems high enough to make possible a continuous dyeing process. The requisite amounts of dye and solvent (2·5% and 17% respectively on the weight of the material) could be applied by a Pad–Roll system, and fixation achieved by passing the material through a solution corresponding to the steady state, so that it would not remove dye or solvent from the fabric. By using a temperature higher than 60°C., much smaller amounts of solvent would be needed, and the time required to get adequate dye fixation could be reduced to a few minutes, which is essential for a satisfactory continuous process. The obvious extension to printing must also be a practical proposition, for it has already been applied to the Vigoureux printing of wool.

In order to test the efficiency of benzyl alcohol as a carrier of this dye for triacetate under practical conditions, a length of Tricel locknit fabric (kindly supplied by Mr. H. C. Olpin of British Celanese Ltd.) was dyed at 60°C. on a jig for 30 min. in a solution saturated with benzyl alcohol. The cloth was uniformly dyed to a deep colour, and the fastness, according to the S.D.C. Mechanical Washing Test A, was 5.

Small samples of Terylene fabric also were dyed to a heavy depth with this dye after being boiled for only 30 min. in a dyebath containing sufficient benzyl alcohol to saturate the solution. A similar experiment without the alcohol gave only a faint tint to the cloth.

MISCELLANEOUS

The colour of cellulose triacetate dyed in presence of benzyl alcohol appears very slightly bluer than that dyed in presence of *n*-butanol. Fearing that the commercial dye might contain small amounts of a blue component having different dyeing

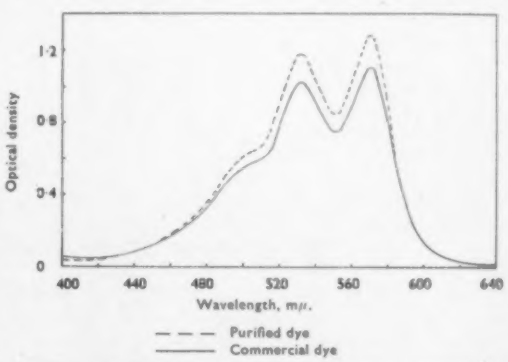

FIG. 7— Absorption Spectra of 1:4-Diamino-2-methoxyanthraquinone (20 mg./litre) and Duranol Red X3B 300 powder fine (100 mg./litre) (peaks of maximum absorption at 532·$_5$ and 570·$_5$ mμ.)

properties in different alcohols, the optical absorption spectrum of the dye was compared with that of a purified specimen, as described in an earlier section. The curves reproduced in Fig. 7 show the close similarity, and also constitute a record of the spectrum of this dye.

The change in colour may, therefore, be due only to a difference in degree of dye aggregation brought about by using another solvent.

The effect of water-insoluble solvents such as diethyl phthalate and tri-*n*-propyl phosphate in acting as carriers for dyeing triacetate has been ascribed to their swelling action on the fibres[3]. Examination of the behaviour of cellulose triacetate fibres under the microscope, however, did not reveal any visible increase in swelling on applying benzyl or butyl alcohol.

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(*MS. received 20th July 1957*)

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[1] Peters, L., and Stevens, C. B., *Dyer*, **115**, 327 (1956); J.S.D.C., **72**, 100 (1956).
[2] Fern, A. S., and Hadfield, H. R., J.S.D.C., **71**, 840 (1955).
[3] Vickerstaff, T., *Hexagon Digest*, (20), 7 (Oct. 1954).
[4] Mellor, A., and Olpin, H. C., J.S.D.C., **71**, 817 (1955); Olpin, H. C., and Wood, J., *ibid.*, **73**, 247 (1957).

Discussion

Dr. J. F. GAUNT: In this paper, dyeing is assumed to be merely the transfer of dye from dyebath to fibre. Such a simple definition would not be accepted in practice, since a high degree of exhaustion is often an embarrassment, and true dyeing in the commercial sense implies controlled uptake to give maximum fastness of the dye. Are the colorations produced by dyeing at these relatively low temperatures, when the state of aggregation of the dyes is probably different from that when dyeing takes place at 100°C., of equal fastness to dyeings made at higher temperatures? This is particularly important as regards fastness to treatment at higher temperature, e.g. hot pressing, permanent pleating, or severe washing.

Dr. PETERS: In our paper we strove to make a clear distinction between true dyeing and mere transfer of dye from dyebath to fibre. The latter was referred to as "strike" on to a liquid surface layer of solvent, whereas the subsequent penetration of the fibre is considered to be the true dyeing phenomenon. To that end we defined "dye fixed on the fibre" as that which could not be removed by the scouring process and which survived the washing test described.

The following fastness tests were carried out by Mr. E. Stead of the Technical Service Department of the Yorkshire Dyeware & Chemical Co. Ltd. After 120 hr. exposure, our solvent-dyed material had a light-fastness rating of 5, identical with that of cellulose triacetate dyed with 2·5% Serisol Fast Red X3B 300 (C.I. Disperse Red 11) at 90°C. for 90 min. Similar results were obtained for a sample of Terylene dyed as described. Marking-off on to viscose rayon or cellulose triacetate after dry pressing at 190°C. for 1 min. or at 200°C. for 2 min. was the same, and there seemed to be no change of colour. Steaming at 20 lb./sq.in. for 15 min. or at 15 lb./sq.in. for 20 min. led to similar marking-off with both dyeings. The fastness to soaking in water at room temperature for 24 hr. was the same for both dyeings.

Dr. GAUNT: Other problems which suggest themselves are the difficulty of removing the solvent from the fibre: any unusual odour associated with the dyed material would be a serious commercial handicap.

Dr. PETERS: There seemed to be no difficulty in removing benzyl alcohol and no unusual odour is associated with the dyed material.

Dr. GAUNT: Is the overall levelness of colour dyed in presence of solvents affected by the evenness of uptake and penetration of the solvent?

Dr. PETERS: We believe that true equilibrium is reached even after only 30 min. at 60°C., and that this causes the evenness of uptake and penetration of the solvent and the levelness of the dyeing.

Mr. B. KRAMRISCH: It has been shown that butanol and benzyl alcohol, which are solvents for disperse dyes, facilitate their absorption by cellulose triacetate. Can these solvents be used for reversing the process, i.e. as stripping agents?

Dr. PETERS: Some degree of stripping with butanol or benzyl alcohol is possible, but trichloroethylene seemed better. We therefore used it exclusively as the stripping agent for estimating dye on the fibre.

Mr. KRAMRISCH: Certain organic compounds suggested as carriers to facilitate the uptake of dyes by cellulose triacetate are stated to be liable to have a deleterious action on the light fastness of some disperse dyes, particularly anthraquinone blues. Does this happen with butanol and benzyl alcohol?

Dr. PETERS: The reply to Dr. Gaunt (above) concerns a disperse red, but there seems no reason why the results should not be similar for anthraquinone blues.

Dr. G. H. LISTER: The lecturer states that he has had difficulty in obtaining a satisfactory thermodynamic interpretation of the results. May this not be due to the fact that equilibrium has not been reached? Whatever the rate of dyeing at the surface, the effective dyeing rate will be controlled by the slowest process, which is probably site-to-site migration, and this will be extremely slow at low temperatures. It is not impossible to obtain a satisfactory surface dyeing which will pass the fastness test used, but penetration inside the fibre may be poor. Has any examination been made of cross-sections of the material dyed at low temperatures?

Dr. PETERS: The difficulty is not that equilibrium is not reached in presence of solvent: we are quite convinced that it is. What we are not sure of is whether equilibrium is reached in absence of solvent even after the prolonged dyeing times we allowed.

TABLE IV

Concn. of carrier, g. of active material per 100 g. of oven-dry fibre ...	0	9·0	21·0
Increase in weight after centrifuging (*a*), %	16·5	22·5	31·9
Retained increase in weight after drying (*b*), %	0	9·3	21·7
Amount of water contained in centrifuged fibre—			
By subtraction (*c*), %	16·5	13·2	10·2
By direct measurement (*d*), %	16·4	13·2	9·8

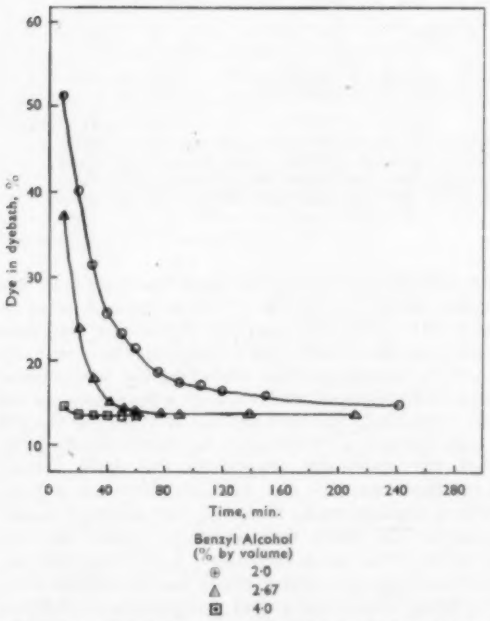


FIG. 8.—Effect of Concentration of Benzyl Alcohol on Rate of Dyeing of Cellulose Triacetate with Duranol Red X3B (C.I. Disperse Red 11) at 60°C.

Our theory, that the action of the solvent is to hasten the arrival at, but not to alter, the final equilibrium state, was supported by the data for dyeing at 60°C. in presence of varied amounts of benzyl alcohol (Fig. 8).

Some data for dyeing at 80°C. in presence of varied amounts of benzyl alcohol are slightly different and have to be confirmed. If established, they would contradict that assumption, and make rigorous thermodynamic analysis difficult.

As to the question of site-to-site migration, it seems unwise to assert *a priori* that it is necessarily slow at low temperatures; we believe that the presence of solvents such as we describe markedly accelerates the process.

Mr. J. S. WARD: We are very much inclined to the theory that many carriers operate by acting as the diffusion media within the fibre. In our own work with carriers on cellulose triacetate (see below) we have shown that the absorption of carrier by the fibre is achieved at the expense of the water originally present. The carrier, being a better dye solvent than water, then allows diffusion to take place more rapidly.

Weighed oven-dry samples of Tricel C staple fibre were treated in dispersions of Carrier LB (a phenolic-type carrier under development by Courtaulds Ltd.) in 40 vol. at 95°C. for 30 min., centrifuged at 1000*g* for 5 min., and weighed again (increase in weight (*a*), Table IV). The samples were then dried to constant weight at 105°C. and weighed again (retained increase in weight (*b*)). The amount of water (*c*) contained in the centrifuged treated fibre was determined by subtraction of (*b*) from (*a*).

In a further experiment samples of Tricel C which had been dyed in the presence of Carrier LB and dried were soaked in distilled water, centrifuged at 1000*g* for 5 min., weighed, and dried to constant weight at 105°C. (amount of water retained after centrifuging (*d*)).

Dr. PETERS: The data supplied by Mr. Ward are very gratifying in that they support the theory that the main source of the affinity of dyeing is the gain in entropy of the adsorbed water molecules when they are displaced from the fibre by the dye molecules. Their preliminary displacement by solvent molecules, which in turn are more easily displaced by the dye molecules, would account for the catalytic action of the solvent.

Dr. R. P. SHELDON*: In the application of Duranol Red X3B (C.I. Disperse Red 11) via organic-solvent solution at 80°C., can the authors say what extent of penetration of the fibre is achieved?

Dr. PETERS*: We have not yet examined cross-sections of cellulose triacetate dyed under the above conditions, but the results are so like others we have examined that it seems fairly certain that full penetration has occurred.

* Communicated.

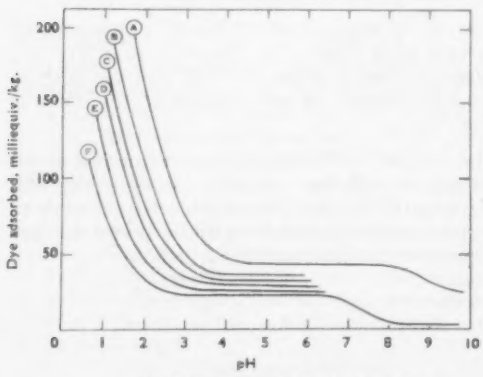
Some Observations on the Dyeing of Nylon with Mixtures of Acid Dyes

E. ATHERTON, D. A. DOWNEY, and R. H. PETERS

Recently published work on the uptake of acid dyes by nylon is discussed. The concept of anion activity gradient as the driving force for diffusion of dyes in nylon is applied to the uptake of mixtures of acid dyes and the problem of compatibility. It is shown that the properties of single acid dyes in finite dyebaths may be represented by "compatibility indices" and that incompatibility is entirely determined by liquor ratio.

Nylon is formed by the condensation of hexamethylenediamine and adipic acid to give a fibre-forming polymer whose molecules have numerous amide groups along the chains, which terminate in either carboxyl, amine, or acetamido. Because of these polar groups, nylon bears some resemblance to wool, and the mechanism of dyeing with acid dyes might be expected to be associated with the amine end-groups in the fibre. Dye-adsorption experiments have shown, however, that this comparison cannot be pushed too far, for the uptake of acid dyes by this fibre as a function of dyebath pH gives rise not only to a simple sigmoid curve but, in addition, at low pH values to a curve which rises steeply as the pH is further decreased. In Fig. 1 are reproduced graphs of dye uptake plotted against pH for baths of high dye concentration. It was considered that under such conditions the maximum dye uptake was obtained [1].

These curves indicate that the mechanism of dyeing is more complex with nylon than with wool.



(A) Naphthalene Red J (C.I. Acid Red 88)
(B) Naphthalene Orange G (C.I. Acid Orange 7)
(C) Solway Blue R (C.I. Acid Blue 47)
(D) Lissamine Fast Yellow 2G (C.I. Acid Yellow 17
(E) Azo Geranine 2G (C.I. Acid Red 1)
(F) Solway Blue B (C.I. Acid Blue 45)

FIG. 1.— Variation of Equilibrium Dye Uptake with Change in pH [1]

Nevertheless, if the portion of the curve at the higher acidities (i.e. pH $< 2{\cdot}5$) is ignored, since at such pH values the dyebath conditions are more acid than those met with in practice, the remaining curve is similar to that obtained for wool, being essentially sigmoid and reaching a maximum as the pH is lowered. The mechanism of dyeing in the pH range above 3 may therefore be stated briefly to be that the carboxyl groups in the fibre adsorb hydrogen ions, and the dye ions are then able to attach themselves to the positively charged amino groups. The ionic link which is formed by this process is the most important factor determining the total amount of dye which can be adsorbed by the fibre. Since the amino group content of nylon is limited and may be determined by titration of a solution of the fibre with mineral acid, an upper limit is set to the amount of dye which can be taken up by nylon. The saturation value of the fibre is a function of the fibre alone, and should not be affected in any way by the composition of the dyebath. This theory predicts the existence of a stoichiometric relation between the numbers of equivalents adsorbed of dyes having different basicities, a fact which is, within approximate limits, borne out by experiment. The agreement between theory and experiment is such as to leave little doubt about the correctness of the postulated dyeing mechanism, but departures from stoichiometry occur and are in themselves interesting.

Some of the saturation values (plotted in terms of equivalents) are found to be lower than the amine end-group content of the fibre, while others are above it. In Fig. 1 the graphs illustrate the range of variation which occurs. Similar deviations from stoichiometric behaviour have been observed by McGrew and Schneider [2] and Remington and Gladding [3]. These were attributed to the difficulty of fitting a polysulphonated dye molecule to the fibre in such a way that all potential ionic links could be formed. Further evidence of the variability of saturation value has been obtained by Lemin [4], who has shown, in studying the uptake of the free acids of the dyes Naphthalene Red EA and Solway Blue B in the absence of foreign electrolyte, that the former has a saturation value

of 37 and the latter of 28 milliequivalents per kilogram of fibre. Uptake in excess of the amount equivalent to the amino group content tends to occur the more readily the fewer sulphonic acid groups there are in the dye molecule. The nature of this adsorption process has been discussed in detail by O'Briain and Peters [5].

In addition to its dependence on the degree of sulphonation of the dye, the extent to which this "overdyeing" (or dye uptake in excess of the amine groups) occurs depends on the concentration of the dye as well as the pH of the bath. This means that the dye uptake and hence the titration curves determined under conditions of high dye concentration are not suitable for physicochemical studies of the equilibrium of the dye which is associated with the amino groups. The dependence of overdyeing on dye concentration has been investigated by the present authors [6].

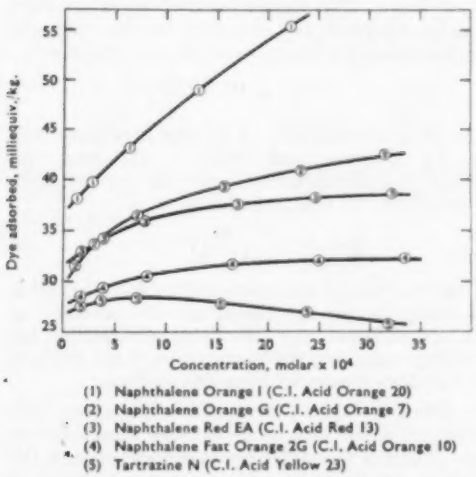


FIG. 2— Variation of Equilibrium Dye Uptake at pH 3·0 with Change in Dyebath Concentration

Adsorption isotherms in which dye concentration was varied were determined at a fixed pH of 3. Some of the results are reproduced in Fig. 2, from which it can be seen that strong adsorption of dye at the low dye concentrations is followed by additional adsorption as the concentration increases, and that this tails off to a lesser or greater extent depending on the affinity and the basicity of the dye. The monobasic dyes show large, and the dibasic dyes small, effects, whereas with the tribasic dye Tartrazine N dye uptake decreases as the concentration increases, presumably because the dye is salted out. These curves were interpreted as showing that, at the lower dyebath concentrations, the dye is adsorbed on the amino groups, but that, as the dyebath concentration increases, overdyeing occurs as a result of the increase in the concentration of undissociated dye acid. It was hoped that the ordinate obtained by extrapolation back to zero dyebath concentration would give the saturation value of the fibre with respect to dyeing on the amino groups. The values so obtained confirmed the previous conclusion that the saturation values were higher the lower the basicity of the dye. However, practical dyeing is carried out with low concentrations of dye acid in the bath, and hence attention must be devoted to dyeing on the amino groups.

For the practical dyeing of nylon the low saturation values for acid dyes caused considerable difficulty. Until the recent introduction of "basic nylon", very great depths of colour could not be obtained with acid dyes, but a much greater source of practical difficulty was the incompatibility of dyes in admixture. For any fibre to take up dye, the outer surface in contact with the dyebath should adsorb a high concentration of dye. Subsequent dye uptake occurs by diffusion of dye molecules from this surface layer to the inside of the fibres, the surface layer being replenished from the bath. Again the relatively low saturation value of nylon puts a well defined limit to the amount of dye which can be adsorbed on the outer surface of the fibres, and in the dyeing of a mixture of acid dyes competition will therefore exist between the various components of the mixture for the available dyeing sites at the surface. The success which any given dye achieves in competition of this kind depends on a number of factors. From the theoretical point of view, the affinities of the various dye anions together with their concentrations and basicities will determine the proportion of sites occupied by each. In practice, additional factors such as liquor ratio must be considered, since, for a given final depth of dyeing, the smaller this ratio the greater will be the variation in the concentration of dye in the bath during the process. From what has been said already, it is apparent that the seemingly simple dyeing mechanism involves a number of complications, which, although not obviously exercising an overriding influence in dyeing from a single-component dyebath, nevertheless can have a profound effect when mixtures of dyes are employed.

To consider one feature only, if the dyeing is being carried out at a pH at which one component of a pair shows no tendency to dye in excess of the amino-group uptake, while the other is capable of overdyeing, then the second component will be taken up in excess, the extent depending upon a number of factors such as the diffusion coefficients relating to the amino-group dyeing and to overdyeing and the variation of these coefficients with temperature. Because of the complexity of the problem of explaining the observed dyeing behaviour of mixtures of dyes, it is unlikely that any precise index of performance can be assigned to a dye, which will adequately express its power to compete in a mixture under any set of dyebath conditions which can occur in practice. It is already obvious, and has in fact been shown by Abbot, Crook, and Townend [7], that simple experimental parameters such as time of half dyeing are not adequate for this purpose. They showed that, under conditions of temperature and liquor ratio such that the times of half dyeing of Tartrazine N and Lissamine Red 7BP were 1 and 2 min. respectively when the dyes were applied singly, if the dyes

were mixed in equal proportions in the dyebath these times became 11·25 and 3·25 min. (Table I). Thus any predictions based upon the relative dyeing speeds of the components considered singly would give erroneous conclusions as to their behaviour in mixtures.

TABLE I

Earlier Finite-dyebath Data[7]

Dyebath—(1) 0·5% Lissamine Red 7BPS (C.I. Acid Violet 5) +(2) 0·5% Tartrazine NS (C.I. Acid Yellow 23)

Time (min.)	Dyebath Exhaustion (%) (1)	(2)	log (Dyebath Concn.) (1)	(2)
1·5	34	7	1·819	1·968
3·0	48	15	1·716	1·929
7·5	74	34	1·415	1·819
11·25	89	50	1·041	1·699
15·0	95	62	0·699	1·580

The object of the present paper is to consider in some detail the factors which determine compatibility of acid dyes in binary mixtures and to show that it is possible to define a compatibility index which will represent the ability of a particular dye to compete with other dyes for uptake by nylon. However, before we discuss compatibility we must mention some of the previous work on the dyeing of nylon with mixtures of acid dyes from infinite dyebaths, as this is the most convenient starting point.

The simplest approach to the problem is to consider two dyes and apply Fick's laws to the diffusion of each, assuming that the surface of the fibre is shared by them according to their affinities. The diffusion of the dyes from this surface layer is then governed by the concentration gradient of each dye. The equations expressing Fick's laws may be solved mathematically, and the quantity of each dye calculated as a function of time and individual diffusion coefficients D_1 and D_2. The concentrations of dye in the surface layer are equal to the concentrations of dye in the fibre after infinite time of dyeing, since this layer is assumed to be in equilibrium with the external dyebath. Solution of the Fick's-law equations leads, for a substance of circular cross-section of radius r, to Hill's equation; i.e. the quantities $Q_{1,t}$ and $Q_{2,t}$ of the dyes adsorbed after time t are given by (i)—

$$Q_{1,t} = Q_{1,\infty}[1-0{\cdot}692\ (e^{-5{\cdot}785D_1t/r^2} + 0{\cdot}190e^{-30{\cdot}5D_1t/r^2} + \ldots)]$$

$$Q_{2,t} = Q_{2,\infty}[1-0{\cdot}692(e^{-5{\cdot}785D_2t/r^2} + 0{\cdot}190e^{-30{\cdot}5D_2t/r^2} + \ldots)]$$

Thus the ratio of the quantities of the two dyes taken up at any one time is given by (ii)—

$$\frac{Q_{1,t}}{Q_{2,t}} = \frac{Q_{1,\infty}[1-0{\cdot}692\ (e^{-5{\cdot}785D_1t/r^2} + 0{\cdot}190e^{-30{\cdot}5D_1t/r^2} + \ldots)]}{Q_{2,\infty}[1-0{\cdot}692\ (e^{-5{\cdot}785D_2t/r^2} + 0{\cdot}190e^{-30{\cdot}5D_2t/r^2} + \ldots)]}$$

This ratio is of importance, since changes in its value are shown as a change of colour during dyeing. For a compatible pair of dyes a plot of $Q_{1,t}$ against $Q_{2,t}$ should be a straight line, but this can be so only if the diffusion coefficients of the two dyes are the same. If Fick's law is obeyed, it follows that the compatibility is determined by the rate of dyeing, since rate of dyeing and diffusion coefficient are interdependent in such systems. This is not true in practice, however, and it seems that the assumption which forms the basis of Fick's law, viz. that the driving force for the diffusion of each dye is its own concentration gradient, needs to be modified. A possible modification might be to assume that the diffusion coefficient in Fick's equation depends on concentration. This could be written—

$$S_1 = -\ D_1(C_1)\frac{\partial C_1}{\partial x} \qquad \text{(iii)}$$

for a single dye, or—

$$S_1 = -\ D_1(C_1, C_2)\frac{\partial C_1}{\partial x} \qquad \text{(iv)}$$

for dye 1 of concentration C_1 in the presence of a concentration C_2 of dye 2. S_1 is the "diffusion flux" of dye 1. Unfortunately, such an approach is difficult to make, since the functional dependence of the diffusion coefficient on concentration is unknown and can be determined only by experiment.

A very much simpler approach is to assume the diffusion coefficient to be constant and redefine the driving force. The simple concentration gradient could be replaced, for example, by the chemical potential gradient $\partial\mu/\partial x$; μ is now written as—

$$\mu = \mu^\circ + \boldsymbol{R}T \ln \frac{\theta}{1-\theta}$$

at any point in the fibre. A simpler expression was used by Atherton and Peters[8], who took the gradient of anion activity to be the driving force for diffusion. In this instance—

$$S = -\ D\frac{\partial}{\partial x}\left(\frac{\theta}{1-\theta}\right) \qquad \text{(v)}$$

θ is the fraction of sites occupied by the dye and is considered to be calculated as the number of gram-molecules at any one point divided by the saturation value and the basicity z; x is the distance into the fibre measured from the surface.

In defining the fractional saturation of the fibre by dyes of differing basicity serious complications arise. Much of the difficulty is connected with the definition of a dyeing site, a concept which is necessary before thermodynamics can be applied to the system. So long as attention is confined to monobasic dyes, the "dyeing site" may be regarded as a region in the fibre in the vicinity of a single charged amino group. For a dibasic dye this must be extended to a region which includes two charged groups. Although each of these pictures can be visualised in isolation, it is difficult to see the situation when dyes of different basicities are adsorbed simultaneously. Further, it is found impossible to apply to such a system, where the so-called "dyeing site" could be used for adsorption of dyes of differing basicity, rigid statistical-mechanical reasoning. For the purpose of deriving an equation describing the adsorption of dyes by nylon, Atherton, Downey, and Peters[6] assumed that the total number of available sites could be grouped according to the basicity of the dyes. This led to the equation for the chemical potential given above.

The diffusion equation defined above is particularly suitable for the analysis of the simultaneous uptake of two dyes by nylon, since allowance is made for the effect of the presence of one dye on the

diffusion flux S of the other. Thus, for the simultaneous diffusion of the two dyes into the fibre, two equations may be written—

$$S_1 = \frac{dQ_1}{dt} = -D_1 \frac{\partial}{\partial x}\left(\frac{\theta_1}{1-\theta_1-\theta_2}\right) \quad \text{(vi)}$$

$$S_2 = \frac{dQ_2}{dt} = -D_2 \frac{\partial}{\partial x}\left(\frac{\theta_2}{1-\theta_1-\theta_2}\right) \quad \text{(vii)}$$

in which S_1 and S_2 are the fluxes of dyes 1 and 2. Since both θ_1 and θ_2 are functions of x, these equations may be differentiated to give—

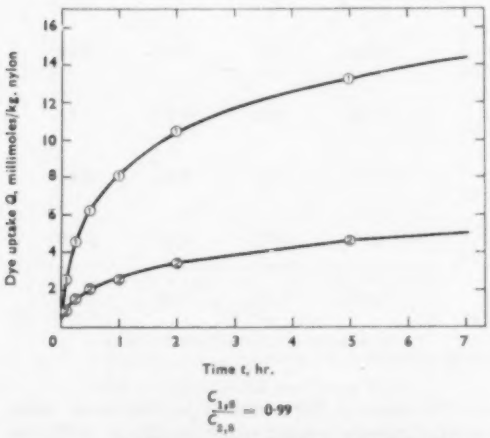
$$\frac{dQ_1}{dt} = -D_1 \frac{(1-\theta_2)\frac{\partial\theta_1}{\partial x} + \theta_1\frac{\partial\theta_2}{\partial x}}{(1-\theta_1-\theta_2)^2} \quad \text{(viii)}$$

$$\frac{dQ_2}{dt} = -D_2 \frac{(1-\theta_1)\frac{\partial\theta_2}{\partial x} + \theta_2\frac{\partial\theta_1}{\partial x}}{(1-\theta_1-\theta_2)^2} \quad \text{(ix)}$$

These two equations predict that, for dyebaths in which all dye concentrations are constant throughout dyeing, the rate of uptake of one is proportional to that of the second according to the following equation—

$$\frac{dQ_1/dt}{dQ_2/dt} = \frac{D_1 z_1 C_{1,s}}{D_2 z_2 C_{2,s}} \exp\left[\frac{-(\Delta\mu_1^\circ - \Delta\mu_2^\circ)}{RT}\right] \quad \text{(x)}$$

where $\Delta\mu_1^\circ$ and $\Delta\mu_2^\circ$ are the standard affinities of the dyes and $C_{1,s}$ and $C_{2,s}$ their concentrations in the dyebath.



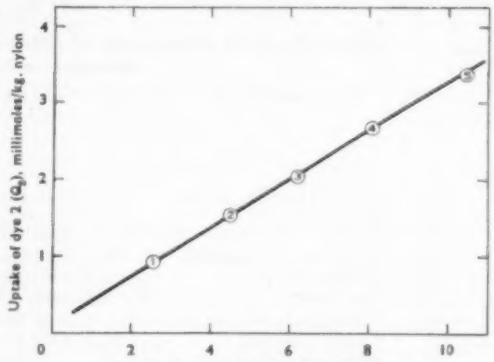
$$\frac{C_{1,s}}{C_{2,s}} = 0.99$$

(1) Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)
(2) Lissamine Red 6B (C.I. Acid Violet 7)

FIG. 3— Rate-of-dyeing Curve from Infinite Dyebath at 75°C. for Binary Mixture

Thus, if complications such as overdyeing or deviation from stoichiometry are absent, the uptake of binary mixtures of acid dyes by nylon from dyebaths of constant composition is controlled by the affinities, diffusion coefficients, basicities, and concentrations of dyes in the dyebath.

In order to check the validity of this equation the uptake rate curves of nine acid dyes in binary mixture (21 in all) were determined from dyebaths of pH 3·2 containing 1 g. of commercial dye per litre [8]. In each case the amount of one dye on the fibre after any dyeing time was plotted against the amount of the second dye present at the same time. An example of a typical pair of uptake rate curves and the derived ratio plot is shown in Fig. 3 and 4. In every case studied, a straight-line ratio plot was obtained, in general confirmation of equation (x).



$$\frac{C_{1,s}}{C_{2,s}} = 0.99$$

Dye 1— Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)
Dye 2— Lissamine Red 6B (C.I. Acid Violet 7)

Time of Dyeing
(1) 5 min.
(2) 15 min.
(3) 30 min.
(4) 60 min.
(5) 120 min.

FIG. 4— Relative Dye Uptake from Infinite Dyebath at 75°C. containing a Binary Mixture

A number of other checks were carried out, the most significant being a cyclical computation: the uptake ratio equation may be written—

$$\frac{dQ_1/dt}{dQ_2/dt} = \frac{D_1 z_1 C_{1,s}\exp(-\Delta\mu_1^\circ/RT)}{D_2 z_2 C_{2,s}\exp(-\Delta\mu_2^\circ/RT)} = \frac{A_1}{A_2} \quad \text{(xi)}$$

where A_1 and A_2 are regarded as parameters for the dyes concerned. Similarly, for dyes 2 and 3 ratios of the rates may be written as A_2/A_3. It follows, then, that for dyes 2 and 3 ratios of the rates A_1/A_3 could be derived by multiplication of the results for dyes 1 and 2 and for 2 and 3. All the data obtained in this work were treated in this manner. The results (Table II) show that, in general, the agreement between calculated and measured values is good, implying that the behaviour of acid dyes in mixtures can be represented by single terms in assessing competition under infinite-dyebath conditions.

It is highly significant that compatible dyeing behaviour was found in every experiment carried out on a binary mixture. This was undoubtedly associated with the fact that the composition of the dyebath was kept constant throughout the dyeing operation in the experiments reported. It may be said on this evidence that the very marked degree of incompatibility which is observed in practice is due to the economic necessity for applying dyes from dyebaths whose volume is small enough to prevent wastage of dye in the final dyebath. Thus, in studying incompatibility under

TABLE II

Cyclic Check on Consistency of Relative Rates of Uptake of Dye from Binary Mixtures in Infinite Dyebath

	Dye Combinations	*Colour Index* No.	$\frac{dQ_1}{dt}/\frac{dQ_1}{dt}^{\bullet}$	$\frac{dQ_2}{dt}/\frac{dQ_2}{dt}^{\bullet}$	$\frac{dQ_1}{dt}/\frac{dQ_2}{dt}$ (Product of preceding columns)	$\frac{dQ_1}{dt}/\frac{dQ_2}{dt}$ (Measured directly)•
(1)	Naphthalene Scarlet 4R	C.I. Acid Red 18				
(2)	Solway Blue A	C.I. Acid Blue 69	0·71	0·53	0·38	0·26
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Naphthalene Scarlet 4R	C.I. Acid Red 18				
(2)	Solway Blue A	C.I. Acid Blue 69	0·71	4·92	3·49	3·52
(3)	Tartrazine	C.I. Acid Yellow 23				
(1)	Naphthalene Scarlet 4R	C.I. Acid Red 18				
(2)	Solway Blue BN	C.I. Acid Blue 45	0·62	0·52	0·32	0·26
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Naphthalene Scarlet 4R	C.I. Acid Red 18				
(2)	Solway Blue BN	C.I. Acid Blue 45	0·62	5·53	3·43	3·52
(3)	Tartrazine N	C.I. Acid Yellow 23				
(1)	Azo Geranine 2G	C.I. Acid Red 1				
(2)	Solway Blue A	C.I. Acid Blue 69	0·94	0·53	0·50	0·53
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Azo Geranine 2G	C.I. Acid Red 1				
(2)	Solway Blue A	C.I. Acid Blue 69	0·94	4·92	4·62	4·92
(3)	Tartrazine N	C.I. Acid Yellow 23				
(1)	Azo Geranine 2G	C.I. Acid Red 1				
(2)	Solway Blue BN	C.I. Acid Blue 45	0·83	0·52	0·43	0·53
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Azo Geranine 2G	C.I. Acid Red 1				
(2)	Solway Blue BN	C.I. Acid Blue 45	0·83	5·53	4·59	4·92
(3)	Tartrazine N	C.I. Acid Yellow 23				
(1)	Lissamine Red 6B	C.I. Acid Violet 7				
(2)	Solway Blue A	C.I. Acid Blue 69	0·50	0·53	0·27	0·21
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Lissamine Red 6B	C.I. Acid Violet 7				
(2)	Solway Blue A	C.I. Acid Blue 69	0·50	4·92	2·46	2·43
(3)	Tartrazine N	C.I. Acid Yellow 23				
(1)	Lissamine Red 6B	C.I. Acid Violet 7				
(2)	Solway Blue BN	C.I. Acid Blue 45	0·44	0·52	0·23	0·21
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Lissamine Red 6B	C.I. Acid Violet 7				
(2)	Solway Blue BN	C.I. Acid Blue 45	0·44	5·53	2·44	2·43
(3)	Tartrazine N	C.I. Acid Yellow 23				
(1)	Lissamine Red 7BP	C.I. Acid Violet 5				
(2)	Solway Blue A	C.I. Acid Blue 69	1·84	0·53	0·98	1·20
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				
(1)	Lissamine Red 7BP	C.I. Acid Violet 5				
(2)	Solway Blue BN	C.I. Acid Blue 45	2·77	0·52	1·44	1·20
(3)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17				

• Gradients of the linear Q_1–Q_2, etc. plots

practical conditions attention must be focused upon the changes of concentration which occur in the dyebath, using the concepts already developed to explain uptake of mixtures from infinite dyebaths.

It is possible to put the earlier equation for uptake ratio into a more suitable form for discussing dyeings from finite dyebaths, by taking into account the condition that the total amount of dye present in the system remains constant. This may be expressed—

$$VC_{1,s} = V_0C_{1,s} - Q_1m$$

or—

$$C_{1,s} = {}_0C_{1,s} - \frac{Q_1}{R} \qquad \text{(xii)}$$

where ${}_0C_{1,s}$ is the initial concentration of dye 1 in the dyebath, V is the volume of the dyebath, m is the mass of fibre, and R is the liquor ratio. A similar equation is obtained for dye 2. Differentiating these equations leads to—

$$R\,dC_{1,s} = -\,dQ_1$$

$$R\,dC_{2,s} = -\,dQ_2 \qquad \text{(xiii)}$$

Substitution of (xiii) into equation (xi) gives on rearrangement—

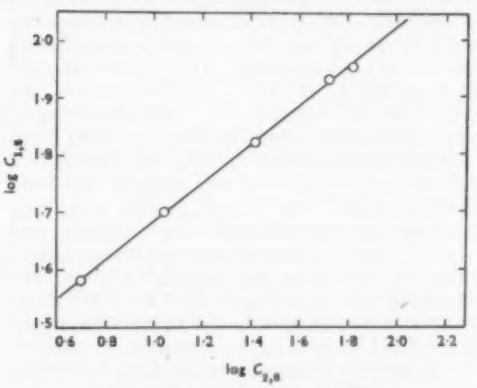
$$\frac{dC_{1,s}/C_{1,s}}{dC_{2,s}/C_{2,s}} = \frac{d\ln C_{1,s}}{d\ln C_{2,s}} = \frac{D_1z_1}{D_2z_2}\exp\left[\frac{-(\Delta\mu_1^{\circ} - \Delta\mu_2^{\circ})}{RT}\right] \qquad \text{(xiv)}$$

Equation (xiv) signifies that a plot of $\ln C_{1,s}$ against $\ln C_{2,s}$ would be linear throughout the whole course of dyeing from a finite dyebath. This conclusion depends upon the validity of the initial

equation, and in order to appreciate the limitations of the logarithmic equation it is necessary to consider the assumptions made in its derivation. Equations (vi) and (vii) are intractable unless assumptions are made as to the degree of saturation of the outer fibre surface. Under the conditions employed in the previous studies of behaviour in infinite dyebaths, the dyeing surface was effectively saturated with dye. This meant that, to a close approximation—

$$\theta_1 + \theta_2 \simeq 1 \text{ or } \theta_1 \simeq (1 - \theta_2) \text{ and } \theta_2 \simeq (1 - \theta_1) \quad \text{(xv)}$$

and the simplified form of equation (x) which has already been discussed was obtained. Equations (x) and (xiv) will be correct if the outer surface of the fibre may be considered to be saturated with dye throughout the dyeing process. Under these conditions linear logarithmic plots should be obtained from finite dyebath experiments, irrespective of the changes of dyebath composition which might occur. However, if changes of dyebath composition take place during dyeing, changes in the adsorbed layer must occur, since this layer is assumed to be in equilibrium with the dyebath. Thus it is to be expected that, in dealing with mixtures in which one component exhausts much more rapidly and completely than the other, a perfectly linear logarithmic plot will not be obtained over the whole range.



Dye 1— Tartrazine N (C.I. Acid Yellow 23)
Dye 2— Lissamine Red 7BP (C.I. Acid Violet 5)

FIG. 5— Logarithmic Plot from Earlier Data[7]

In order to illustrate the kind of plot which may be obtained, even when the dyes concerned are incompatible, the data of Abbot, Crook, and Townend [7] have been plotted on a logarithmic basis in Fig. 5, and it can be seen that the result is a good straight line.

The criterion of compatibility may now be considered in more detail. In practice, for a pair of dyes to be compatible they should build up on tone, or effectively behave as would a single dye. This condition would be secured if the uptake ratio were constant. For this to be true in (xiv) the ratio of the dyebath concentrations of the two dyes concerned would have to be constant. Thus the criterion for compatibility, under the conditions to which equation (xiv) applies, is that the ratio of dyebath concentrations shall not vary during dyeing.

There remains to be considered the conditions prevailing when the total amount of dye is insufficient to saturate the outer surface of the fibre at all stages of the dyeing process. The above derivation of (xiv) is no longer correct, since it is not now possible to assume that (xv) holds. It may be shown, however, that the assumptions (xv) are not the only ones which will enable the two factors containing the first derivatives in (viii) and (ix) to be cancelled. Another assumption which will lead to the same result is that θ_1/θ_2 is constant. This was not appreciated when (viii) and (ix) were derived in an earlier paper [9] for the case of infinite dyebaths, but it is of great importance in the treatment of finite dyebaths. Thus it is now established that the validity of (xiv) extends to the case where insufficient dye is present to saturate the outer surface of the fibre but where the ratio of the amounts of the two dyes in the adsorbed surface layer is a constant independent of dyeing time. The condition for compatibility in (xiv) is that $C_{1,s}/C_{2,s}$ is constant, and so it is necessary that the ratios of the amounts of dyes on the surface and also in the bath should both be constant throughout dyeing, if compatible behaviour is to be observed under conditions of high dyebath exhaustion.

In order to obtain a numerical value for the competing power or compatibility of a dye, equation (xiv) may be rewritten—

$$\ln C_{1,s} = k \ln C_{2,s} + M \quad \text{(xvi)}$$

where k, the *compatibility ratio*, is given by—

$$k = \frac{D_1 z_1}{D_2 z_2} \exp\left[\frac{-(\Delta\mu_1^\circ - \Delta\mu_2^\circ)}{RT}\right]$$

which is constant, and M also is a constant. Equation (xvi) may now be rewritten—

$$\frac{C_{1,s}}{C_{2,s}^{\,k}} = e^M = N \text{ (a constant)} \quad \text{(xvii)}$$

Thus, for the ratio of dyebath concentrations to be constant in a finite dyebath it is necessary that—

$$k = 1$$

or—

$$D_1 z_1 e^{-\Delta\mu_1^\circ/RT} = D_2 z_2 e^{-\Delta\mu_2^\circ/RT} \quad \text{(xviii)}$$

which is a similar criterion to that deduced by Meggy [9] for compatibility, although his method of derivation is open to criticism.

In (xviii) each side of the equation is characteristic of one dye in the mixture and may be regarded as the compatibility index of that dye. When the ratio k of compatibility indices is equal to unity, the pair of dyes should be compatible. The greater the departure from unity, the less compatible will the pair be. It is obvious that a convenient way of measuring the compatibility ratio for a pair of dyes is to determine the slope k of the logarithmic plot obtained from a single experiment in a finite dyebath. For this purpose the dyebath concentration must be sufficiently high to ensure a straight-line plot being obtained (since it is necessary to

TABLE III

Combination of Diffusion-coefficient and Affinity Data in Form required for Calculation of Compatibility Index

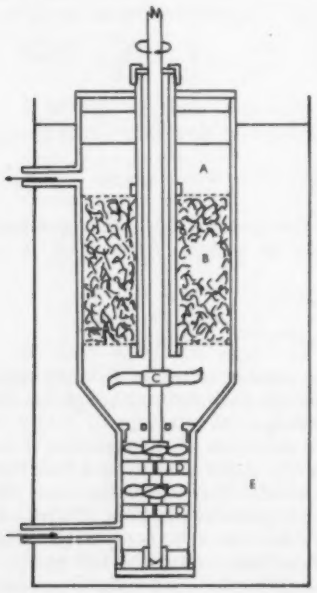
Dye	*Colour Index* No.	D/r^2 ($\times 10^5$)	z	exp* ($\times 10^3$)	$\frac{Dz \exp^*}{r^2}$ ($\times 10^9$)
Tartrazine N	C.I. Acid Yellow 23	1·43	3	1·18	5·08
Solway Blue A	C.I. Acid Blue 69	3·28	2	0·794	5·21
Lissamine Red 6B	C.I. Acid Violet 7	1·19	2	2·75	6·57
Azo Geranine 2G	C.I. Acid Red 1	3·18	2	1·59	10·1
Lissamine Yellow 2G	C.I. Acid Yellow 17	2·50	2	2·09	10·45
Solway Blue BN	C.I. Acid Blue 45	4·38	2	1·41	12·35
Lissamine Red 7BP	C.I. Acid Violet 5	0·78	2	10·0	15·6
Naphthalene Fast Orange 2G	C.I. Acid Orange 10	7·00	2	1·35	18·9
Naphthalene Scarlet 4R	C.I. Acid Red 18	1·94	3	4·47	26·1

* $\exp^* = e^{-\Delta\mu^\circ/RT}$

maintain the outer surface of the fibre saturated with dye). It is also possible to calculate the compatibility indices of a number of dyes from data presented in previous publications [6, 8] (Table III). These values may be compared with the practical data obtained in the present work.

EXPERIMENTAL

The rate-of-dyeing determinations were carried out in the apparatus shown diagrammatically in Fig. 6. It was made of stainless steel, all joints being welded except the top and bottom bearings, which were screwed to the body of the machine, these joints being sealed with hard rubber gaskets. In the initial measurements trouble was experienced in obtaining level dyeings. This was traced to streamline flow through the fibre plug and was overcome by addition of a slightly curved paddle attached to the main shaft at the taper in the outer casing. This arrangement supplied a liquor circulation in a direction at right angles to that given by the pump. With this modification level dyeings were obtained with all the dye mixtures which were studied.



A Dyebath
B Staple fibre
C Paddle— to break up streamlines
D Straightening vanes
E Thermostatic bath

FIG. 6— Apparatus for Measurement of Rate of Dyeing

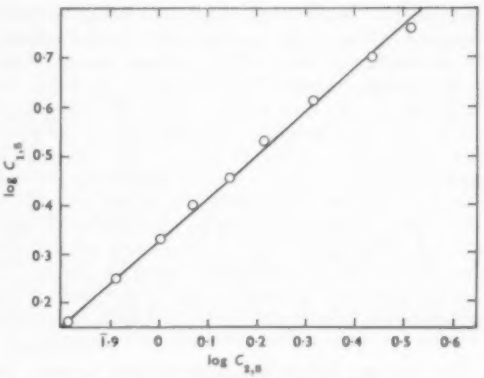
The method of measurement was to pipette 350 ml. of distilled water into the dyebath and add 2 ml. of formic acid (2%). Stock solutions of the dyes to be used in the experiment (5 ml. of each) were added to the dyebath, and the volume was brought up to 400 ml. The dyebath was allowed to reach a steady temperature (75°C.), and the cage containing the fibre (4 g.) was lowered into the dyeing vessel, adjustment of the rate of stirring of the dye liquor being made so as to maintain rapid circulation through the fibre plug and through an optical cell connected to the side-arms of the vessel.

The optical cell was placed in the measuring beam of the Cary recording spectrophotometer, and the optical density of the dye solution was measured as a function of time of immersion of the fibre. For this purpose the recording chart of the instrument was run at a known speed, and the measurements were confined to the two wavelengths corresponding to maximum absorption of the dyes concerned, these wavelengths being selected alternately. Thus two intermittent traces were generated corresponding to the optical density–time curves at the two wavelengths. In cases where the absorption spectra of the dyes did not overlap, these curves were converted directly into the rate-of-dyeing curves of the two dyes by multiplying the ordinates by conversion factors relating concentration to optical density. In cases where there was a significant overlap of the absorption spectra, allowance had to be made for this before the individual rate-of-dyeing curves could be plotted. This was done by the method described by Vickerstaff [10].

At the completion of the dyeing, the pH of the dyebath was measured, and was found to vary between 2·9 and 3·1 depending upon the dyes used. The total dye concentrations used in the dyeings were selected arbitrarily, with the proviso that the amount of dye present was always less than that corresponding to complete saturation of the fibre.

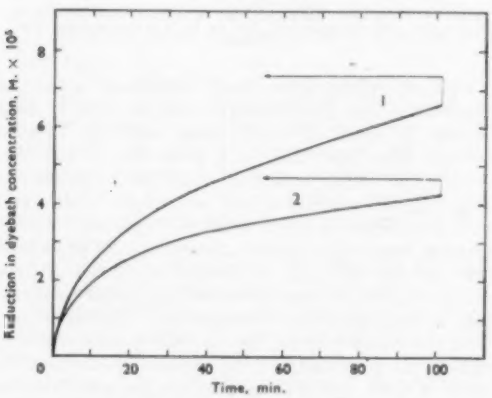
RESULTS AND DISCUSSION

The rates of uptake of seven binary mixtures were measured in the manner described previously at a liquor ratio of 100:1. The combinations of the dyes were chosen because of the suitability of their absorption spectra; i.e. their wavelengths of maximum absorption were far enough apart to give two well separated peaks when the dyes were mixed together. Fig. 7 gives typical curves in which the loss of dyebath concentration for each of two components is plotted against time. The data so obtained were treated in the manner described earlier: the logarithm of the concentration of dye 1 in the bath was plotted against that of dye 2, and in most cases straight lines resulted. Two examples of such plots are given in Fig. 8 and 9. The slopes of the lines so obtained give, according to equation (xvi), the values of k, the compatibility ratio, and these experimental values are given in Table IV (last column) along with values of k arrived at by two other methods.



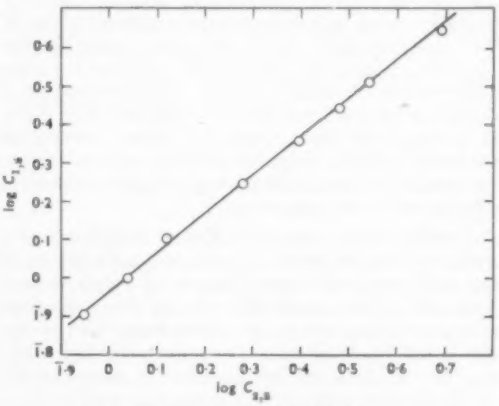
Dye 1— Solway Blue BN (C.I. Acid Blue 45)
Dye 2— Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)

FIG. 8— Logarithmic Plot for Dyeing of Binary Mixture from Finite Dyebath at 75°C.



↑—— Initial concentration of dye
Dye 1— Solway Blue BN (C.I. Acid Blue 45)
Dye 2— Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)

FIG. 7— Dyeing Rates for Binary Mixture at 75°C.



Dye 1— Azo Geranine 2G (C.I. Acid Red 1)
Dye 2— Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)

FIG. 9— Logarithmic Plot for Dyeing of Binary Mixture from Finite Dyebath at 75°C.

TABLE IV

Comparison of Values of the Compatibility Ratio k derived by Three Methods

	Dye Combination	*Colour Index* No.	Basicity (z)	Values of k calculated from*— (a)	(b)	(c)
(1)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17	2	3·15	0·40	0·56
(2)	Naphthalene Scarlet 4R	C.I. Acid Red 18	3			
(1)	Solway Blue BN	C.I. Acid Blue 45	2	1·74	0·47	0·53
(2)	Naphthalene Scarlet 4R	C.I. Acid Red 18	3			
(1)	Solway Blue A	C.I. Acid Blue 69	2	3·30	1·03	1·00
(2)	Tartrazine N	C.I. Acid Yellow 23	3			
(1)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17	2	1·46	0·85	1·23
(2)	Solway Blue BN	C.I. Acid Blue 45	2			
(1)	Azo Geranine 2G	C.I. Acid Red 1	2	1·13	0·97	0·96
(2)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17	2			
(1)	Azo Geranine 2G	C.I. Acid Red 1	2	1·34	0·82	0·92
(2)	Solway Blue BN	C.I. Acid Blue 45	2			
(1)	Lissamine Fast Yellow 2G	C.I. Acid Yellow 17	2	1·42	2·01	1·50
(2)	Solway Blue A	C.I. Acid Blue 69	2		See Table III	

* (a) Infinite-dyebath data— $k = \frac{dQ_1/dt}{dQ_2/dt} \times \frac{C_{2,s}}{C_{1,s}}$ (b) Diffusion coefficient and affinity— $k = \frac{D_1 z_1}{D_2 z_2} \exp\left[\frac{-(\Delta\mu_1^\circ - \Delta\mu_2^\circ)}{RT}\right]$

(c) Finite-dyebath data— $k = \frac{d \ln C_{1,s}}{d \ln C_{2,s}}$

In general, the agreement between predicted and measured values of k is satisfactory and confirms the reasoning given earlier. There are residual discrepancies, however, which are attributable to a number of possible causes. The affinities from which the compatibility indices were calculated were measured with highly dilute desorbing liquors and fibre dyed so that θ was rarely greater than 0·6. These considerations would therefore not apply to the more highly concentrated dyebaths occurring in the early stages of dyeing. Also, the diffusion coefficients used in Table III were determined by measurements of uptake from concentrated infinite dyebaths, and this, too, could account for some of the residual discrepancies.

That dyeing behaviour in mixtures depends on concentration may be shown by analysing the results given in Table II for rates of uptake from infinite dyebaths. Equations (xi) and (xvi) show that, if the listed values of $(dQ_1/dt)/(dQ_2/dt)$ are divided by $(C_{1,s}/C_{2,s})$, the compatibility ratio k is obtained. Values obtained in this way relate to much higher concentrations than occur in the finite-dyebath or desorption experiments. They are compared in Table IV with the k values obtained from finite-dyebath experiments and those calculated from affinity and diffusion data. It is apparent that there are great differences between the infinite-dyebath results and the others, particularly where dyes having different degrees of sulphonation are concerned.

In these latter cases the effect of increasing total dyebath concentration is to favour adsorption of the dye with the lower degree of sulphonation. This effect is a good example of the difficulties encountered in any quantitative treatment of the uptake of dye mixtures. The known affinity values for the two dyes predict a certain partition of the available fibre surface, but under the conditions of competition prevailing in the dyebath, the dye of lower degree of sulphonation can more readily be accommodated in any partly occupied region of the fibre surface than can the other dye. To illustrate this, we may regard the fibre surface as a point lattice, a part of which is shown in Fig. 10, and consider competition between disulphonated and tetrasulphonated molecules— (*a*) If two tetrasulphonated molecules are placed on the lattice in any position, it is possible to accommodate four disulphonated molecules on the remaining sites. (*b*) If two disulphonated molecules are placed as shown, no tetrasulphonated molecule can be accommodated, and a further six disulphonated molecules will be adsorbed. It may be noted as evidence for the importance of this effect that, in the first three calculations in Table III, the disulphonated dye monopolises the fibre at high concentrations, even though its affinity is lower in each case than that of the trisulphonated dye, which it is able to exclude from the fibre.

It would seem, nevertheless, that the conditions of the infinite-dyebath experiments were extreme as regards the competition effects. For finite baths, log–log plots indicate little change in slope as the concentration or depth increases. Since so many combinations, even those which are incompatible, give straight-line log–log plots, one might be justified in assuming that the ratio of the surface occupied by the two dyes does not substantially alter during the dyeing. Obviously, this must be an approximation, and it is to be expected that deviations from linearity do occur if the affinities or the basicities of the two dyes are very different.

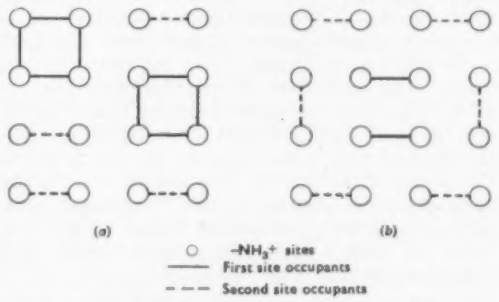


FIG. 10— Schematic Representation of Competition between a Di- and a Tetra-sulphonated Dye for the Charged Dyeing Sites of Nylon

Non-linear plots have been obtained with the monobasic dye Naphthalene Orange G (C.I. Acid Orange 7) used in conjunction with the dibasic Solway Blue BN (C.I. Acid Blue 45). When this occurs, the rather restricted conditions assumed in deriving the equations are no longer valid, and such deviations as occur must be expected. It is at present impossible to solve the equations presented here for the diffusion of binary mixtures of dyes except under the conditions of (*a*) surface saturation or (*b*) constant surface sharing. This, however, does not detract from the use of the compatibility ratio k as a parameter for choosing compatible pairs of dyes, but it does prevent the quantitative assessment of the extent of incompatibility when the compatibility indices of the two dyes are very different.

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Discussion

Mr. H. R. HADFIELD: The equations developed in this paper very concisely define the properties of a nylon-reserving agent. Has the lecturer any comment to make on the extension of the work to this extreme case of incompatibility?

Professor PETERS: The essential feature of a reserving agent is that it should be strongly adsorbed on the outer surface of the nylon fibre without diffusing into the fibre to any great extent. It does not seem that the present work would make possible new concepts of the action of reserving agents, since, as indicated in the paper, predictions of k from diffusion and affinity data become less accurate the greater the degree of incompatibility.

Mr. H. A. TURNER: Far too little is known about the "strike" region in the early stages of dyeing, and I wonder which of the following alternatives is likely to be the more useful—

(1) The outer layer of the fibre contains dye at a high concentration (not saturation) dependent on the concentration of the bath and the affinity, and from this layer further diffusion into the fibre takes place.

(2) The outer layer of the fibre, with dyes of substantial affinity, is saturated, and more dye from the bath can enter only as dye from the saturated layer diffuses further into the fibre. Here in the early stages of dyeing the concentration of the dyebath would not be reflected in the concentration of the "strike" layer but in the depth of the saturated layer.

Is there any information available which would help to decide between the alternatives?

Professor PETERS: I agree that more knowledge of the early stages of dyeing would be valuable, particularly in diffusion studies. As far as the mathematics is concerned, there is no difference between points (1) and (2), since theoretically we never get a completely saturated layer. I think that we must investigate both ideas brought up by the questioner. The "strike layer" will be dependent on the affinity and the diffusion coefficient, and it is likely that dyes of very high affinity may have a very slow diffusion rate and hence give a very thin layer of high dye concentration. Dyes of low affinity may show a very rapid diffusion rate, and hence a layer will not be obvious. Between these extremes may come dyes of reasonably high affinity but also reasonably fast diffusion rates, and hence it may be these dyes which exhibit the highest strike. More work is necessary to show whether this is so.

Mr. I. GAILEY: The mathematical treatment contained in this paper is based on the hypothesis that there are two independent species of dye competing for a limited number of adsorption sites in a fibre. Recent papers[9-11] have shown that frequently the individual dyes in a binary mixture combine with one another to form complexes. Has the effect of such complex formation been considered in developing the theory described in this paper? What effect would the existence of complexes have on the theory and its mathematical treatment?

Dr. ATHERTON: The effect of complex formation has not been considered in developing the present theory, since complications of this kind do not arise to any significant extent with simple acid dyes of the type studied. In other cases where such complexes are formed, the present theory would give no more than an approximate guide to behaviour, since the thermodynamic treatment would not apply rigidly to the solution phase.

Dr. L. PETERS: In the equation defining compatibility ratio—

$$k = \frac{D_1 z_1 \exp(-\Delta\mu_1^\circ/RT)}{D_2 z_2 \exp(-\Delta\mu_2^\circ/RT)}$$

the Ds can be written in the form—

$$D = \exp(-\Delta E^*/RT)$$

where ΔE^* is an activation energy of diffusion into the fibre. Hence k is determined (apart from the basicity) by the difference between the energy required to promote diffusion and the change in energy at equilibrium. Is this difference equal to the activation energy of *desorption*? Thus, can one express the compatibility coefficient k in terms of a diffusion coefficient for diffusion out of the fibre?

Professor PETERS: The implication of this suggestion needs careful consideration in view of the uncertainty regarding the diffusion coefficients used in the present work. As indicated in the paper, breakdowns of Fick's equation (which are known to have differential effects on diffusion coefficients for migration into and out of the fibre) must occur. No attempt to characterise compatibility in terms of activation energy of desorption could be made with available data, but this might indeed be a useful field for further investigation.

Investigations into the Dyeing of Continuous-filament Nylon with Disperse and Anionic Dyes

H. W. PETERS and J. C. TURNER

The nature of the variations in continuous-filament nylon and their influence on dyeing behaviour are explained. By the use of a special fabric containing yarn differing in physical and chemical properties by known and controlled amounts, the sensitivities to such variations of many dyes for nylon have been assessed. These results appear in the appendix in tabular form, and are intended to help the dyer to select suitable dyes, by indicating their abilities to cover yarn irregularities. New and current dyeing methods are discussed, and suggestions are made for improved uniformity. Laboratory investigations have shown which new methods offer most prospects of success, and also where more detailed investigation will be of value.

1. INTRODUCTION

Outstanding among the factors which determine the use of a particular dye on a particular fibre is the ability of that dye both to colour the goods uniformly and to provide adequate fastness for the proposed end-use. These requirements are not always reconcilable on continuous-filament nylon, whether as yarn or as fabric. This paper endeavours to explain the underlying difficulties, to describe the behaviour of the various dye classes on nylon, and to suggest directions in which progress in the wider application of faster dyes may most readily be made.

At the present time, by far the greater proportion of continuous-filament nylon, whether in yarn, fabric, or garment form, is dyed with disperse dyes. This is so for two major reasons: firstly, disperse dyes are easily applied; and secondly, they are generally superior to other dye classes in levelling properties, and in their ability to cover any variations which may exist within and between nylon yarns. However, although disperse dyes are satisfactory for such articles as nylon stockings, whose wear life is shorter than that of the dye, their moderate fastness to wet treatments, and often to light, makes them less suitable for a number of other uses. In particular, when fashion trends demand medium and heavy depths, the poor washfastness of disperse dyes is most noticeable. There is continuous and increasing commercial pressure for the use of faster dyes on nylon, and it is the business of the yarn producer, the throwster, the fabric manufacturer, the dyer, and the dye manufacturer to satisfy this need. This means that the co-operation of all concerned is essential, and that those whose responsibility is commercial must be aware of what can and what cannot yet be achieved.

Mention has already been made of the coverage of yarn irregularities by disperse dyes and of the inferior ability of other types of dyes to provide uniformity of colour. This, however, is a general view of the situation, and this paper gives a more detailed description of the behaviour of a large number of individual dyes towards yarn irregularities similar to those found in commercial yarns and fabrics.

Before discussing dye behaviour it is appropriate to consider briefly the principal factors upon which dyeing uniformity depends. These are—

(*a*) Yarn uniformity
(*b*) Dye selection
(*c*) Dyeing method.

By (*a*) is meant identity of chemical and physical properties both within and between yarns. Variations in either or both of these are capable of causing dyeing variations, and while all efforts are made by the yarn producer to ensure yarn uniformity, no textile fibre is ever completely free from irregularities. In addition, it is possible at many stages of yarn processing and fabric manufacture to introduce further variations which affect dyeing performance, and the dyer is therefore presented with considerable problems. It is the purpose of this paper to describe these problems and to provide some guidance in overcoming them, but it would be untrue to pretend that the work described is a complete solution. Its main purpose is to draw attention to dyeing difficulties and to make available information that is both of practical value and able to serve as a starting point and a stimulus for further investigations.

2. THE NATURE OF VARIATIONS IN CONTINUOUS-FILAMENT NYLON

The dyeing characteristics of nylon are influenced by two properties of the yarn [1–4]—

(i) Amine end-group content
(ii) Physical structure.

Variation in amine end-group content causes variation in both rate of dyeing and equilibrium uptake of anionic dyes [3]. The latter property can be used as a measure of amine end-group content by dyeing to equilibrium with a mono- or a disulphonated dye of relatively low molecular weight. A more accurate method is to perform an acid-base titration [5], this being necessary for strict production control. Equilibrium dyeing with Solway Blue BN

(C.I. Acid Blue 45) is often used as a qualitative test to confirm or disprove the presence of amine end-group inequalities between yarns.

Chemical variations in yarn are thus controllable to a high degree by the yarn producer, and segregation can be, and is, effected on the basis of amine end-group measurements. If this segregation is maintained after the yarn leaves the producer, then dyeing variations with anionic dyes, due to chemical irregularities, will be kept to a minimum, if not virtually eliminated.

Whereas the picture of amine end-group variation is relatively simple, the problems of variation in physical structure are much more complex. The former is, as described, controllable within practical limits by routine tests, but at present, despite activity in all sections of the trade, it is not yet possible to ensure absolute uniformity of physical structure.

It is not the aim of this paper to attempt to discuss in great detail the nature of these physical structure variations, but two factors are involved [2]—

(1) Overall degree of order (crystallinity)

(2) Degree of longitudinal orientation.

These two properties of the physical structure affect the rate of dyeing, in that increase in either will bring about a decrease in dyeing rate. This alteration of rate of dyeing is clearly of great importance to the dyer, and since different dyes are not affected to the same extent by the same degree of variation in physical structure, we have classified a large number according to their sensitivities to known and controlled variations.

It is appropriate first to consider where these physical structure variations may be introduced. Both crystallinity and degree of orientation are determined to a considerable extent during yarn manufacture [2, 6].

It is known [2] that variations in tension, within or between yarns, occurring during yarn processing, fabric manufacture, and finishing are also capable of introducing variations in dyeing rate, unless the extension produced is not permanent and is removed before dyeing takes place. This is not always possible, as, for instance, the yarn(s) affected may be held under constraint in a fabric; or the variation in tension may have been caused by differential shrinkage during twist-setting of a package. In the latter case the yarn will have been set under varying tensions, and the inside of the package may dye at a rate different from the yarn on the outside. Variations in physical structure may also occur during heat setting, both from tension variations present, or from temperature fluctuations (which may occur e.g. in the preparation of crimped yarn by the false-twist method).

From the dyer's point of view, these irregularities, wherever introduced, cause rate-of-dyeing differences, and, depending on the dyes and dyeing methods used, variations in appearance of the dyed yarn or fabric may result. Since rate-of-dyeing variations caused by physical structure differences do not affect the equilibrium dye uptake of nylon, it is theoretically possible to avoid differences in depth by allowing dyeing to continue until a true state of equilibrium is reached. This is not a practical answer, since the majority of dyes do not come to equilibrium in a sufficiently short time.

In addition to differences in rate of dyeing caused by variations in physical structure, other physical factors also play some part in producing non-uniformity. Two of these are denier and lustre variations. Palmer and Munden [1] have shown that the dyeing rate of a nylon filament may be considered to be inversely proportional to the square root of the denier (the lower the filament denier, the greater the specific surface area, and the higher the dyeing rate). This effect is independent of any associated orientation differences between the filaments whose deniers differ.

Lustre variations may be connected with differences in internal physical structure, in surface characteristics, or in both. If only differences in surface characteristics exist, then, although identical amounts of dye may be present, the apparent depths of colour may be different because of the different light-reflecting properties of the yarn surface.

To summarise, both chemical and physical structural characteristics of nylon determine its dyeing behaviour. The relative importance of these two properties varies with the particular dye used, but, as chemical properties are controllable by the yarn producer, the principal causes of dyeing irregularity are differences in physical structure within and between nylon filaments, which introduce differences in rate of dyeing.

3. IDENTIFICATION OF CAUSES OF DYEING IRREGULARITY

The preceding section has outlined the nature of the irregularities which continuous-filament nylon may contain. While it is generally possible to determine whether chemical or physical (or both) differences are responsible, say, for the appearance of warp stripiness in woven fabric, it is seldom possible to determine precisely where, or at what stage, these variations were introduced. Again, presence of amine end-group differences presents a simpler problem than does the presence of physical structure differences, since amine end-group content is controlled by the merge system. Physical structure, however, can be altered significantly, e.g. by differences in tension and temperature, and variations in these factors between yarns can introduce variations in rate of dyeing.

A series of simple tests has been developed which makes it possible in general to decide what type of variation is present: the faulty fabric is dyed with four dyes, as follows—

(*a*) DURANOL BRILLIANT BLUE BN (C.I. Disperse Blue 3)— The dyebath contains 2% of dye and 1 ml. of Dispersol VL (ICI) per litre. Dyeing is started at 40°C., the temperature raised to 85°C., and dyeing continued at this temperature for 45 min. Under these conditions, this dye is typical of the level-dyeing disperse dyes, and covers both chemical and physical variations.

(*b*) SOLWAY BLUE BN (C.I. Acid Blue 45)— This dye, when dyed for 4 hr. at 100°C. on nylon, in a

bath containing 5% dye and 4% formic acid (90%), is very sensitive to amine end-group differences, but covers physical structure variations.

(*c*) DURAZOL BLUE 2R (C.I. Direct Blue 71)—Dyeings are made with 2% dye (on weight of fabric), 3% acetic acid (30% vol./vol.), entering at 40°C., raising to 100°C., and continuing for 1 hr. The dyeing rate of Durazol Blue 2R, whose large molecule is tetrasulphonated, is, under these dyeing conditions, very dependent on the physical structure of nylon [1, 2]. It is also, being an anionic dye, sensitive to chemical variations.

By comparing these three dyeings, it is generally possible to determine whether dyeing irregularity is due to physical or chemical variations. As an example, it may be imagined that (*a*) and (*b*) show no signs of irregularity, but that (*c*) reproduces the original fault. It is then clear that the dyeing variation is caused by a physical abnormality, which has altered the rate of dyeing.

(*d*) MULTAMINE BLACK B (ICI)—Where dyeing (*a*) with Duranol Brilliant Blue BN is similar in appearance to (*b*) and (*c*), then lustre variations may be suspected, and these may be confirmed by carrying out a fourth dyeing, with 10% Multamine Black B (on weight of fabric) and 1 ml. of Dispersol VL (ICI) per litre. Dyeings are made at 85°C. for 45 min. This black-dyed fabric will show no yarn variations, except that of lustre.

These tests will define the causes of dyeing differences. It is, however, difficult to proceed further by determining at which stage, or stages, in the history of the yarn or fabric such irregularities have been introduced, with the exception of such obvious gross faults as the presence of partially drawn yarn, the mixing of twist-set and non-twist-set yarns, or irregularities in fabric construction.

Since, wherever physical variations are introduced into yarn, they are of the same nature, knowledge of the sensitivity of dyes to such variations is necessary. Such knowledge may then be translated into terms of dye selection. For this work it was essential to have some yardstick by which dye behaviour could be assessed. This was provided in the form of a woven fabric containing in its warp in succession across the piece one-inch bars of—(i) a normal yarn (control), (ii) a yarn differing in amine end-group content, but otherwise similar to the control, and (iii) a yarn, as near to the control in amine end-group content as possible, but differing physically in having a lower degree of orientation than the control (Table I). It should be emphasised that the magnitude of these deliberately introduced variations is much greater than one would expect to find in a commercial fabric, but this does not affect the validity of the comparative ratings, nor alter the value of the work as a guide to the dyer.

TABLE I

Yarn	Amine End-group Content (micro-equiv./g.)	Draw Ratio
(i) Control	41	Normal
(ii) Chemically different	30	Normal
(iii) Physically different	42	Low

Thus, it is possible by dyeing this fabric with a particular dye to obtain a semi-quantitative measure of its sensitivity towards the yarn variations, by comparison with a set of dyed controls. These controls are the dyes (*a*)–(*c*) above, and subsequent dyeings have been rated relative to the assessments made on these three (Table II).

We have refrained from making an assessment in a more quantitative form (e.g. on the S.D.C. Grey Scale 1–5 ratings), since we feel that it would be wrong to attempt to put this work on so strictly quantitative a basis.

This experimental fabric also enabled us to make comparative studies of the effects of different dyeing methods on the covering of yarn variations. Because of the widespread use of disperse dyes on continuous-filament nylon, the work and results relating to their application to the experimental fabric are reported and discussed separately from the work with other dyes, which perhaps arbitrarily (but in accord with a main purpose of this paper) have been termed "fast dyes".

4. BEHAVIOUR OF "FAST DYES" TO PHYSICAL STRUCTURE AND CHEMICAL VARIATIONS

Under the broad classification of "fast dyes" are considered the following types—

Soluble dyes for cellulose acetate
Acid wool dyes
Chrome dyes
Direct dyes
Azoic dyes
Vat dyes
Metal-complex dyes (acid- and neutral-dyeing).

Manufacturers' recommendations have been used both as regards actual dyes in that only those which the manufacturers consider of interest on nylon have been used, and dyeing conditions, insofar as these were applicable to laboratory practice. The dyeings have been made on the experimental fabric described in § 3, either in a Marney dyeing machine or in a Smith laboratory dyeing machine, both of which have proved satisfactory for our purpose. The slight variation in liquor ratio resulting from the use of two different machines was shown to be of no significance.

In general, dyebaths were set with 2% dye (on weight of fabric); where exhaustion was low, the 2% is a nominal figure only, but it is shown later that depth of colour, within fairly wide limits, has

TABLE II

Dye (2%)	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
Duranol Brilliant Blue BN	C.I. Disperse Blue 3	Insensitive	Insensitive
Solway Blue BN	C.I. Acid Blue 45	Slightly sensitive	Very sensitive
Durazol Blue 2R	C.I. Direct Blue 71	Very sensitive	Very sensitive

no effect on assessment of sensitivity to yarn variations. Blacks have mostly been dyed in three depths, viz. 2%, 5%, and 10%— here the effect of very heavy depths in covering irregularities is most marked.

Main trends are summarised under the individual dye classes; full details appear in the tables in the appendix to this paper.

Soluble Dyes for Cellulose Acetate

Sensitivity to chemical variations is, in general, rather less than that of acid wool dyes, though greater than that of disperse dyes, because of the presence of anionic solubilising groups. There are also indications that, where additions of acetic acid are necessary to achieve reasonable exhaustion, sensitivity to amine end-group content is increased.

The behaviour of these dyes towards physical structure variations exhibits considerably less ability than disperse dyes to cover them. However, it is possible to select members of reasonably low sensitivity, e.g.—

Solacet Fast Yellow G (ICI)
Solacet Fast Crimson B (C.I. Acid Red 159)
Solacet Fast Blue 2B (C.I. Acid Blue 14)

and these may well be useful where disperse fastness is inadequate, and where some dyeing irregularity may be tolerated. Considered as a complete range, the soluble dyes for cellulose acetate, though inferior in covering properties to disperse dyes, are slightly superior to any corresponding range of acid wool dyes, when compatibility in admixture for production of fashion shades is necessary.

Acid Dyes

This group forms, numerically, the largest class of dyes applicable to nylon and, as might be expected, shows considerable divergence in sensitivity among the individual dyes, particularly to physical structure variations. Almost all the acid wool dyes are markedly affected by variation in amine end-group content; the majority have been assessed as "sensitive" or "very sensitive". There is a much wider spread in sensitivities to physical variations and, as may be seen from Table III, these range from "relatively insensitive" to "very sensitive".

It is possible to select a range of acid dyes which will give fairly good coverage of physical structure variations, but no such range exists which will give as good coverage of chemical irregularities. However, chemical variations are secondary in importance to the physical irregularities, so that where disperse fastness is inadequate, or where a brightness not supplied by disperse dyes is needed, selected acid wool dyes will prove valuable. If, in addition, some stripiness or barriness can be tolerated, or if fabric construction is such as to render any dyeing irregularity less obvious, then the useful range of acid dyes may well be extended.

Chrome Dyes

Chrome dyes possess characteristics similar to those of the acid dyes as regards their sensitivities to chemical and physical variations, and the ratings therefore will indicate which may be used with least risk of non-uniformity. They also possess additional advantages over the acid wool dyes in that their high wash fastness, combined with the ability of several to build up to heavy depths, makes them suitable for blacks, navy blues, and nigger browns, where rate-of-dyeing variations will be less apparent in the dyed fabric.

Direct Dyes

Direct dyes are of less interest on nylon than are the acid wool dyes, being, in general, more sensitive to physical structure variations and having a lower affinity for the fibre. Except for the occasion when use of a direct dye is needed for a particular fashion shade, acid wool dyes will be preferred.

Azoic Dyes

Azoic dyes differ in their sensitivities to physical and chemical variations, but several dyes are potentially of interest because of their low sensitivity to both types of irregularity, good fastness properties, and brightness.

Vat Dyes

Applied conventionally, vat dyes are of little interest on continuous-filament nylon. Most appear sensitive to physical structure variations, in addition to possessing poor light fastness.

Metal-complex Dyes

The older acid-dyeing type (e.g. Neolans (Ciba) and the Ultralans (ICI)) are affected seriously by both chemical and physical structure irregularities. The newer, neutral-dyeing dyes (e.g. Cibalans (Ciba), Irgalans (Gy), and Lanasyns (S)), while showing less sensitivity to amine end-group changes than do the earlier dyes, are extremely sensitive to variations in physical structure. In this respect there is no appreciable difference between different members of the ranges. The rates of dyeing of

TABLE III

Dye (2%)	*Colour Index* No.	Sensitivity* to Variations	
		Physical	Chemical
Lissamine Fast Red B	C.I. Acid Red 37	R.I.	V.S.
Fast Light Orange G	C.I. Acid Orange 10	S.S.	V.S.
Kiton Fast Rubine GRL	C.I. Acid Red 58	M.S.	V.S.
Azo Rubinole 3GP	C.I. Acid Red 57	S.	V.S.
Polar Brilliant Blue GAW	C.I. Acid Blue 127	V.S.	V.S.

* R.I. = Relatively insensitive
S.S. = Slightly sensitive
M.S. = Moderately sensitive
S. = Sensitive
V.S. = Very sensitive

TABLE IV

Dye (2%)	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
Irgalan Rubine RL	C.I. Acid Violet 75	V.S.	M.S.
Cibalan Grey BL	C.I. Acid Black 60	V.S.	M.S.
Lanasyn Yellow 3GL	C.I. Acid Yellow 111	V.S.	S.S.
Ortolan Red G	C.I. Acid Red 221	V.S.	S.S.

metal-complex dyes, particularly of those containing one atom of metal to two molecules of dye, are very dependent on the physical structure of nylon. It is most unfortunate that this should be so, as fastness and building-up characteristics of these dyes on nylon are excellent. Table IV illustrates the uniformly high sensitivity of these dyes to physical structure variations.

5. NEW AND MODIFIED METHODS FOR THE APPLICATION OF "FAST" DYES

While selection of suitable dyes can reduce the incidence of dyeing irregularities, a considerable amount of work has been done, and is still in progress, to test the possibilities of new and modified dyeing methods for covering variations due to different dyeing rates. The two approaches are, to some extent, complementary, but there are features unique to some of the newer methods of dyeing, in that dyes which would not be selected for conventional dyeing techniques may prove suitable for application by these more recent methods.

The work described here has been largely of an exploratory nature, covering a fairly wide field, rather than a more exhaustive investigation of one particular topic, and is considered under the following general headings—

(*a*) High-temperature dyeing
(*b*) Swelling agents and carriers
(*c*) Restraining and retarding agents
(*d*) Pad–fixation techniques
(*e*) Miscellaneous.

(*a*) *High-temperature Dyeing*

Movement of the molecular chains of nylon increases with increasing temperature. Vickerstaff[7] has explained that this will favour the probability, at any given time, that a hole will exist large enough to admit entry of and to accommodate a dye molecule. The rate of diffusion of a dye into the fibre, which is increased by rise in temperature, will be further increased by this effect of temperature on the fibre. Rates of dyeing, and of levelling or migration, are therefore higher at higher temperatures. This much was known, but information on the effects of temperatures above 100°C. on the covering of dyeing irregularities was lacking. The introduction of machines designed to operate at high temperatures has enabled work to be carried out on a semi-bulk scale, as well as laboratory work on small fabric samples. This work is far from complete, but several acid-wool, direct, chrome, and metal-complex dyes have been applied to the experimental fabric, and in some cases to commercial fabrics, on pressure jigs. Although some conflicting points have arisen, the following broad picture is apparent—

1. Some level-dyeing acid wool dyes, and possibly some acid-milling wool dyes, show improved coverage of physical structure variations when applied at high temperature.
2. There are indications that some chromable dyes cover physical structure variations in nylon more completely at temperatures above the boil than at conventional temperatures. Other chrome dyes show less or no improvement, but, as with the acid wool dyes, a more complete and quantitative investigation is required.
3. High-temperature dyeing has not been found to cause any significant improvement in the coverage of physical variations by either the acid-dyeing or the neutral-dyeing metal-complex dyes.
4. No coverage of amine end-group differences is effected at high dyeing temperatures.
5. Rates of dyeing are generally increased, but degrees of exhaustion are, in general, lowered.
6. Improved penetration of closely woven fabrics is obtained at high temperature.

Practical implications of these findings are discussed later, but the subject clearly requires, and will probably repay, a much more exhaustive examination.

(*b*) *Use of Swelling Agents*

A second approach to the problem of opening up the compact physical structure of nylon lies in the use of swelling agents, or, more precisely, in the use of agents which can penetrate the nylon filaments, and enlarge the space available for the entry of dye molecules. Of the various known swelling agents for nylon, phenol has received most attention, commercially, in the U.S.A. and in our laboratory investigations. A process which was devised and practised by Cheney Brothers Ltd., and which has now been taken over by du Pont[8], consists essentially in dyeing, in the presence of phenol and sodium acetate, with selected slow-exhausting acid dyes. This procedure is claimed to reduce faults due to lustre variations and to rate-of-dyeing differences, but the latter are more satisfactorily covered in heavy depths. This is, of course, true of dyeings made without phenol, and may suggest that the technique has limitations in pale–medium depths.

Experiments have been made on the fabric containing known and controlled variations using this procedure with the following dyes (2% depth) recommended by du Pont—

du Pont Milling Red SWB conc. (similar to C.I. Acid Red 167)
Pontamine Scarlet 3B (C.I. Direct Red 39)
du Pont Anthraquinone Iris R (C.I. Acid Violet 43)

These showed a slightly improved cover of physical variations when compared with control dyeings on

TABLE V

Effect on Coverage of Physical Variations of Additions of Formic Acid, Phenol, and Benzyl Alcohol

Dye (2%)	*Colour Index* No.	Control	1% Formic Acid	1% Phenol	1% Benzyl Alcohol
		A*			
Benzyl Fast Red 2G	C.I. Acid Red 111	3	4	2	2–3
Benzyl Fast Red 2B	C.I. Acid Red 115	3–4	4–5	2–3	3
Benzyl Fast Orange G	C.I. Acid Orange 47	3–4	3–4	2–3	3–4
Benzyl Fast Blue R	C.I. Acid Blue 92	3	4	2–3	3
Cloth Fast Blue BR (CAC)	—	3–4	4–5	3	3–4
Benzyl Fast Black B	C.I. Acid Black 24	3–4	4	3	3–4
		B†			
Carbolan Yellow 3G	C.I. Acid Yellow 72	4	4–5	3–4	4
Coomassie Red GS	C.I. Acid Red 116	4	4–5	3–4	4
Carbolan Brilliant Blue 2R	C.I. Acid Blue 140	2–3	3–4	2	2–3
Carbolan Brilliant Green 5G	C.I. Acid Green 28	3	3–4	2	2–3
Coomassie Fast Grey 3G	C.I. Acid Black 48	3	4	3	3

* Controls prepared with 3% acetic acid (30%)
† Controls prepared with 3% ammonium acetate

the same fabric, but there was no effect on coverage of the chemically varying sections.

A second series of dyeings was designed to assess the comparative effects of small additions of formic acid, phenol, and benzyl alcohol to the dyebath. These were added to dyeings of the dyes listed in Table V, and the contrast between the two fabric sections differing in physical structure was rated visually by the use of the S.D.C. Grey Scale for assessment of loss in depth. Control dyeings were made from a bath containing either 3% acetic acid (30%) or 3% ammonium acetate (on weight of fabric).

The trend here shows that, in the amounts used, formic acid is more efficient in promoting coverage of rate-of-dyeing variations (caused by physical structure irregularities) than is phenol or benzyl alcohol. The dyeings made with additions of phenol are, if anything, slightly worse than the controls, but those made with 1% formic acid are slightly better.

Phenol has been similarly of little value in experiments with a metal-complex dye, 1% Irgalan Grey BL (C.I. Acid Black 58). Four dyeings, with 0·1, 0·25, 0·5, and 2% of phenol, and a control dyeing were made. No significant improvement was observed in coverage in any one of the above five dyeings.

When phenol was used as a pretreatment, results were again negative: fabrics were treated at 50°C. for 30 min. in 0·5, 1·0, 2·0, and 3·0% phenol (on weight of fibre) in approx. 100:1 liquor ratio. Dyeings were then made with 1% Irgalan Grey BL on each of the above samples, after rinsing once in cold water. No improvement in coverage of physical variations was observed.

Use in the dyebath of small amounts of the swelling agents, 5-chlorosalicylic acid and *o*-cresotinic acid (3-methylsalicylic acid), has been claimed [9] for the production of deeper colours by increasing the rate of dyeing. Preliminary work, however, indicates that neither has a beneficial effect on coverage of rate-of-dyeing variations, although both are capable of increasing dyeing rate.

(c) Use of Restraining and Retarding Agents

The primary function of both restraining and retarding agents is to reduce dyeing rate. Restraining agents achieve this on nylon by virtue of their anionic character. Under suitable conditions they will occupy some of the sites (terminal amine groups) normally available for anionic dyes and reduce the dyeing rate. This will certainly, with a dye possessing a strong affinity for nylon, help to minimise, say, ending in a jig dyeing. Work has also been done on the use of restraining agents in covering yarn irregularities. Thus, Brooks and Reith [10] claim that the use of Duponol D (DuP) paste (a long-chain fatty alcohol sulphate) with selected acid dyes will give good coverage of physical and chemical irregularities. Their explanation is that an initial level strike is obtained, and that this, in conjunction with the improved migration properties of the dyes, is responsible for the improved coverage.

While this explanation may, in part, be accurate, it does not account satisfactorily for the elimination of rate-of-dyeing differences which must occur in order that any significant improvement should be obtained. It is possible that the assistant has a higher rate of diffusion into nylon filaments than have the dyes, and that it will occupy the most readily available sites, blocking them to the dye molecules, and thus effectively reducing rate-of-dyeing differences.

Our experience is that this assistant, and others of a similar nature, have little effect on the coverage of physical structure variations at temperatures below 100°C. Their principal value is to avoid unlevelness such as ending, by slowing down the rate of dyeing and thus promoting even absorption of colour throughout the piece being dyed. At temperatures above 100°C. there does seem to be a slight improvement in coverage when the assistant is used, but at least part of this improvement is due to the use of the higher dyeing temperature, this having been demonstrated by dyeing at 120°C. without the assistant.

The dyes used in these experiments were the following, being U.K. equivalents of some of the

du Pont dyes recommended for use in the process—

Benzyl Fast Scarlet 3BS (CAC)
Benzyl Fast Red BG (C.I. Acid Red 99)
Chlorantine Fast Red K (C.I. Direct Red 81)
Kiton Fast Rubine GRL (C.I. Acid Red 58)
Kiton Fast Violet R (C.I. Acid Violet 43)
Solway Blue 2GS (C.I. Acid Blue 37)
Alizarine Fast Green G (C.I. Acid Green 25)

Other similar anionic assistants have behaved in much the same manner, so that any real coverage of rate-of-dyeing variations by use of such agents appears to be small. This is not, of course, to minimise their value in promoting levelness, in the sense that the two ends of a piece dye to the same colour, but there seems little prospect of such compounds causing better coverage of physical structure irregularities.

Retarding agents perform a similar function, but differ in that the final exhaustion of the bath is substantially unaffected. Rate of dyeing is reduced, generally, by formation of a dye–assistant complex which is more soluble in water than is the dye alone. With increasing temperature this complex breaks down, and dye is released. Thus the overall dyeing rate can be controlled, but again no marked improvement has been observed in the coverage of rate-of-dyeing variations due to physical structure irregularities. It is, however, agreed that a full and systematic investigation of these two types of assistant has not been undertaken, and that further work may yield more promising results.

(*d*) *Pad–Fixation Techniques*

Under this heading are considered methods of coloration in which fabric is first impregnated with a dye or pigment solution or dispersion by a padding technique, and this is followed by a treatment designed to effect colour fixation and penetration into the fibre.

This approach is one of the most promising for overcoming dyeing irregularities, but it is important that the following principles be followed as closely as is practically possible—

Firstly, the dye or pigment solution or dispersion should have no affinity for the fibre at the padding stage. This means that no differential dyeing of yarns possessing different rates of dyeing can take place. In practice, the nearness with which this requirement can be approached will depend on several factors. Among these are concentration of dye required to give a desired depth of colour, coupled with the temperature needed to keep the dye in solution, and the effect of any restraining agents which may be employed to reduce dye affinity.

Secondly, the fixation stage should, ideally, be capable of causing attachment of dye to fibre without any migration of dye taking place: in other words, the dye must fix in the position in which it is applied by the pad mangle.

Our work has been confined mainly to laboratory dyeings, and consists only of preliminary experiments, designed to give some idea of the relative efficiencies of various fixation techniques, and to enable the prospects of covering irregularities to be assessed.

(i) PAD–STEAM DYEING— In laboratory experiments, both acid and neutral-dyeing metal-complex dyes have been applied to continuous-filament nylon fabric by this technique, with a considerable reduction in warp stripiness over a conventionally dyed control. In these experiments there were no additions of thickening agents to the padding liquor, which consisted generally of a 5% solution of dye plus 1 c.c. of a wetting agent, e.g. Perminal PP (ICI), per litre. Steaming was carried out by placing fabric squares, mounted on a pin frame, in a Paramold stocking-preboarding machine, generally at 25 lb./sq. in. steam pressure for 2½ min. The resultant fastness to washing was in general slightly lower than that of the same dye applied conventionally; but the difference was such as to suggest that a more thorough investigation of steaming conditions would lead to improvement.

(ii) PAD–DRY-HEAT DYEING— Two methods which have been the subject of laboratory experiments are (1) the Thermosol technique of du Pont [11] and (2) the fluid bed method devised by the British Rayon Research Association [12].

In the Thermosol process, fixation of dyes is effected, after padding and a preliminary drying, by exposing the fabric to dry heat in a heat-setting or -curing oven. Temperatures of above 350°F. are commonly used. Disperse dyes are said to be applied successfully to Dacron by this method, but dye fixation is reported to be less successful on nylon.

Experiments with acid milling and neutral-dyeing metal-complex dyes indicate an improvement in coverage of irregularities similar to that obtained by the pad–steam method. Full wet fastness has not been achieved, but a more detailed investigation of fixation conditions is necessary before any firm conclusions are reached.

The fluid bed developed by B.R.R.A. is a most efficient unit for transfer of heat to fabric, and therefore suggests itself as a means of effecting rapid dye fixation. Through the co-operation of the B.R.R.A., dyeings have been made on nylon ribbon in a laboratory-scale fluid sand bed using an acid-wool and a metal-complex dye. Conditions of temperature and time of heating have been found which give wash fastness comparable with that achieved by a normal dyeing, while coverage of irregularities is comparable with that achieved by other pad–fixation techniques.

Details of the dyeings and subsequent wash tests are given in Tables VI and VII.

Tables VI and VII show that the two dyes used are capable of being applied by a fluid-bed technique and that both raising the temperature of the bed and prolonging the time in it (up to 200°C. and 60 sec.) increases the amount of dye fixed, without causing decomposition of dye. Washing tests have been carried out on some of the above dyeings, and on conventionally dyed controls. Ratings (Table VIII) are according to the S.D.C. Grey Scales for assessment of degree of staining and difference in depth.

These results show that, in the case of the acid wool dye, fastness equivalent to that of a conventional dyeing was obtained by fixing, after padding,

TABLE VI

Acid Wool Dye— C.I. Acid Green 28

5% (wt./vol.) Carbolan Brilliant Green 5G8
5% (wt./vol.) Glycerol
0·2% (wt./vol.) Perminal PP (ICI)
Padded at room temperature
Mangle— "Acme" domestic wringer, on highest setting obtainable

Dyeing No.	No. of Times padded	Conditions Fluid Bed Temp. (°c.)	Time in Bed (sec.)	Effect of Water Wash at 50°c.
1	1	120	10	Severe bleed-off of colour
2	1	120	20	Considerable loss of colour, but < (1)
3	2	152	10	Loss of colour, but < (1) and (2)
4	2	152	20	Loss of colour, but < (1)–(3)
5	2	172	10	Less bleed-off than above; final colour deeper
6	2	178	20	Bleed-off < (5); final colour deeper than (5)
7	2	182	10	Some colour loss. Final colour deeper than (5)
8	2	182	20	Some colour loss. Final colour deeper than (7), (6), (5), etc.
9	2	198	10	Final colour appreciably deeper than (7)
10	2	189	20	Final colour deeper than (9) and (8)
11	2	200	40	Final colour deeper than (9) and (10)
12	2	198	60	Final colour deeper than (11)

TABLE VII

Neutral-dyeing Metal-complex Dye (C.I. Acid Black 58)

5% (wt./vol.) Irgalan Grey BL (Gy) (standard strength)
2·5% (wt./vol.) Tinegal W (Gy)
0·2% (wt./vol.) Perminal PP (ICI)
5% (wt./vol.) Glycerol
Padded at room temperature
Mangle— "Acme" domestic wringer, on highest setting obtainable

Dyeing No.	No. of Times padded	Conditions Fluid Bed Temp. (°c.)	Time in Bed (sec.)	Effect of Water Wash at 50°c.
13	2	195	10	Some loss of colour
14	2	195	20	Final colour deeper than (13)
15	2	198	40	Very little colour loss. Final colour deeper than (14)
16	2	198	60	Very little colour loss. Final colour deeper than (15)

TABLE VIII

Wash Tests on Fluid-bed Dyeings

Dyeing No.	Fluid Sand Bed Temp. (°c.)	Time (sec.)	Staining on Nylon	Staining on Cotton	Loss in Depth	Washing Conditions
			CARBOLAN BRILLIANT GREEN 5G			
Control*			5	5	4	
1	120	10	5	5	1	0·2% Soap soln. (2 g./litre) at 60°c. for 30 min.
2	120	20	4–5	5	1	
5	172	10	4	5	1–2	
6	178	20	5	5	2	
11	200	40	5	5	3–4	
12	198	60	5	5	4	
Control*			5	5	2–3	One wash at 50°c. for 10 min. in 0·2% soap soln. to remove any loose colour; then 30 min. at 80–85°c. in 0·5% soap soln.
11	200	40	5	5	2–3	
12	198	60	5	5	3	
			IRGALAN GREY BL			
Control*			5	5	5	
13	195	10	3	5	1–2	0·2% Soap soln. at 60°c. for 30 min.
14	195	20	3–4	5	2	
15	198	40	4	5	2–3	
16	198	60	4	5	3	
Control*			4–5	5	4–5	One wash at 50°c. for 10 min. in 0·2% soap soln.; then 30 min. at 80–85°c. in 0·5% soap soln.
15	198	40	4	5	2–3	
16	198	60	4–5	5	3	

* Conventional dyeing— 2% dye on wt. of fabric

at 198°C. for 60 sec. In the case of Irgalan Grey BL, although the fastness figures for the conventional dyeing do not appear to be achieved by the fluid-bed dyeing, it should be noted that, for the latter, almost identical fastness figures are obtained for both the mild and the more severe washing conditions. It may well be that loose colour is removed by the mild wash and by the first 10 min. scour in the second procedure, which accounts for the loss in depth and the staining, and that no further loss occurs. Thus more satisfactory fixation has probably been achieved than is apparent at first sight.

Coverage of yarn variations was assessed by visual comparison of the appearance of fluid-bed dyeings with that of conventional dyeings using the same two dyes as before, on the fabric containing known and controlled chemical and physical structure variations. Results were promising, in that improvement in coverage was obtained.

(iii) PAD-AND-DEVELOP PROCESS—A third process, due to Ciba [13], consists in padding with a dye solution, similar in composition to the mixture used for the pad–steam process, drying, and finally fixing and developing in a boiling bath containing 1–2 c.c. of 85% formic acid per litre. The basic idea is identical with that of the pad–steam procedure, in that uniform application by padding is followed by a fixation stage, which must, to avoid barriness and stripiness, cause fixation *in situ*. There must also be minimum bleed-off of dye into the developing bath, since, under the acid conditions, this will redye on to the nylon and reveal any inherent irregularities. Experiments have been made, on the laboratory scale, on the lines of the Ciba procedure, using neutral-dyeing metal-complex dyes. Coverage of irregularities is again improved, and the final results are similar to those obtained by other padding procedures. In one or two instances trouble has been experienced when dye has aggregated in the padding liquor, and spotting of solid dye on the fabric has occurred. It will therefore be necessary to consider dye solubility in relation to the desired depth of colour when dyeing by this method (this is true of all padding methods, but has particular relevance here, as any loosely attached dye may bleed-off in the acid bath, and redye on to the fabric). Fastness characteristics have been found to be equal to those of the same dyes applied by conventional means, in pale–medium depths, but some reduction in rubbing fastness has occurred when heavier shades have been produced.

(iv) RESIN-BOUND PIGMENTS—The small amount of laboratory work on padding with pigment-resin binder dispersions indicates that this procedure is capable, under the best conditions, of producing uniformly coloured goods, with excellent all-round fastness—with the restriction that depths greater than medium may be deficient in rubbing fastness.

We have no first-hand experience of the Pad–Roll system of dyeing [14], but it is probable that it will enjoy advantages over conventional methods, similar to those of other padding procedures.

(e) *The Chemnyle Process*

A widely publicised process for the dyeing of continuous-filament nylon, which cannot properly be classified under the previous headings, is that due to the Chemstrand Corporation and described by Hindle [15]. This is known as the Chemnyle process, and is described in the above paper as an attempt to induce anionic dyes to simulate the dyeing behaviour of disperse dyes, in that they are applied to the fibre, not from a true solution, but from a fine dispersion. For this to occur, the anionic dye must be precipitated from solution and then redispersed in a suitable particle size. It is claimed that this is achieved by use of the Chemnyle assistant and a suitable dispersing agent (Triton X–67—Rohm & Haas) at pH 3·5. The nature of the Chemnyle assistant has not been divulged other than to state that it is a cationic agent.

TABLE IX

Depth (% on wt. of fabric)	Sensitivity to Variations: Physical	Chemical
	NAPHTHALENE SCARLET 4RS (C.I. Acid Red 18)	
1	S.S.	V.S.
2	R.I.	V.S.
3	R.I.	V.S.
5	R.I.	V.S.
	XYLENE FAST RED P (C.I. Acid Red 117)	
0·5	S.S.	S.
1	S.S.	S.
2	S.S.	S.
5	R.I.	M.S.
	KITON FAST BLUE CR (C.I. Acid Blue 47)	
1	M.S.	S.
2	M.S.	V.S.
3	S.S.	V.S.
4	S.S.	V.S.
	CARBOLAN BRILLIANT GREEN 5GS (C.I. Acid Green 28)	
1	S.	S.
2	S.	V.S.
3	S.	V.S.
4	M.S.	V.S.
	ERIOCHROME GREY ABE 150 (C.I. Mordant Black 13)	
1	S.S.	V.S.
2	R.I.	V.S.
4	R.I.	V.S.
5	R.I.	V.S.
	IRGALAN BLUE GL (C.I. Acid Blue 166)	
1	V.S.	R.I.
2	V.S.	R.I.
3	V.S.	R.I.
6	S.	R.I.
	CIBALAN BORDEAUX RL (C.I. Acid Violet 71)	
1	V.S.	R.I.
2	V.S.	R.I.
4	V.S.	R.I.
6	M.S.	R.I.

TABLE X

Disperse Dyes

Dye (2%)	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
Dispersol Fast Orange G 300	C.I. Disperse Orange 3	R.I.	R.I.
Duranol Brilliant Blue G 300	C.I. Disperse Blue 14	S.S.	R.I.
Duranol Violet 2R 300	C.I. Disperse Violet 1	M.S.	R.I.
Multamine Brown 2G (ICI)	—	S.	R.I.
Duranol Blue Green B 300	C.I. Disperse Blue 7	V.S.	R.I.
Serisol Fast Orange GD (YDC)	—	R.I.	R.I.
Serisol Fast Pink B	C.I. Disperse Red 3	S.S.	R.I.
Serisol Green BTL (YDC)	—	M.S.	R.I.
Serisol Brilliant Green 3G	C.I. Disperse Green Mixture	S.	R.I.
Serisol Red BGL (YDC)	—	V.S.	R.I.

It should, however, be noted that transforming a soluble dye into a disperse dye is no guarantee of an improvement in its ability to cover physical structure variations in nylon, since several true disperse dyes are not capable of this. Thus, as Hindle says, dye selection will play an important part in the method, and it may quite well be that dye selection alone is the most important factor in minimising irregularity.

6. EFFECT OF DEPTH OF COLOUR ON COVERAGE OF IRREGULARITIES

A further aspect investigated was whether, with "fast" dyes, depth of dyeing markedly affected degree of coverage. Some forty dyes from the various classes were selected and dyed to different depths. The work showed that in general sensitivity is not markedly altered by change in depth. In some cases, as would be expected, heavy depths do decrease the sensitivity to physical variations. Representative examples of the results obtained are given in Table IX.

7. DISPERSE DYES

Disperse dyes are widely used for the dyeing of nylon fabrics, mainly because of their ability to level and cover yarn variations. However, complaints of stripiness have been received even when these dyes are used. Experiments in the laboratory on such stripy fabrics show that, if dyeing or levelling is carried out at the boil with the fabric completely immersed, marked if not complete coverage frequently occurs.

It was decided to investigate the covering properties of a wide range of disperse dyes, using the experimental fabric. Dyeings were first carried out at 85°C. in a 50 : 1 liquor using Dispersol VL (ICI) as dispersing agent. This work showed that disperse dyes vary widely in their covering properties of physical variations, though coverage of chemical variations is, with a very few exceptions, complete. Examples illustrating this point are shown in Table X.

Although 85°C. was taken as the standard dyeing temperature, it is known that under practical conditions dyeing often takes place at a lower temperature. All dyes were, therefore, applied as before, except that the dyeing temperature was lowered to 60°C. In addition, where any specific dye gave poor coverage at 85°C., a further dyeing was made at the boil. This series of dyeings at various temperatures yielded most interesting information.

At 60°C. the majority of disperse dyes are sensitive or very sensitive to physical variations within nylon yarn. At this temperature they have, in general, little if any advantage over normal acid dyes for the covering of physical variations. They do, however, remain relatively insensitive to chemical variations. With increasing temperature

TABLE XI

Temperature-sensitive Disperse Dyes

Dye (2%)	*Colour Index* No.	Coverage of Physical Variations at		
		60°C.	85°C.	100°C.
Artisil Blue SAP	C.I. Disperse Blue 1	V.S.	M.S.	S.S.
Artisil Brown NR (S)	—	V.S.	S.S.	S.S.
Cibacet Brilliant Blue BG new	C.I. Disperse Blue 3	V.S.	M.S.	S.S.
Supracet Green 3G	C.I. Disperse Green Mixture	V.S.	S.S.	—
Supracet Fast Scarlet G	C.I. Disperse Red 19	V.S.	M.S.	S.S.
Serisol Fast Green NB	C.I. Disperse Green Mixture	V.S.	M.S.	S.S.
Setacyl Violet R	C.I. Disperse Violet 1	V.S.	S.S.	S.S.
Setacyl Blue 2GS	C.I. Disperse Blue 1	V.S.	M.S.	M.S.

TABLE XII

Temperature-insensitive Disperse Dyes

Dye (2%)	*Colour Index* No.	Coverage of Physical Variations at		
		60°C.	85°C.	100°C.
Setacyl Discharge Blue GN	C.I. Disperse Blue 30	V.S.	V.S.	V.S.
Serisol Fast Blue BGL	—	V.S.	V.S.	V.S.
Cibacet Violet 5R	C.I. Disperse Violet 10	V.S.	S.	S.
Artisil Orange RFL	C.I. Disperse Orange 21	V.S.	V.S.	S.
Duranol Blue Green B	C.I. Disperse Blue 7	V.S.	V.S.	S.

TABLE XIII

Effect of Dispersing Agents on Covering Properties of Disperse Dyes

(Sensitivity to physical (Phys.) and chemical (Chem.) variations of the nylon)

Dye (2%)	*Colour Index* No.	No Dispersing Agent added		Dyapol PT (YDC) (1 g./litre)		Dyapol M (YDC) (1 c.c./litre)		Soap (2 g./litre)		Dispersol VL (ICI) (1 c.c./litre)		Irgasol DA (Gy) (1 g./litre)		Sandopan WP (S) (1 g./litre)		Tinegal VR (Gy) (1 c.c./litre)	
		Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.
DYEING TEMPERATURE 85°C.																	
Dispersol Fast Orange Brown R	C.I. Disperse Orange 5	S.	R.I.	S.	R.I.	M.S.	R.I.	M.S.	R.I.	S.	R.I.	S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Scarlet GFL	C.I. Disperse Red 43	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Setacyl Red BN (Gy)	—	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Cibacet Red BBS	C.I. Disperse Red 24	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Artisil Red BP	C.I. Disperse Red 24	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Serisol Rubino 3BD	C.I. Disperse Red 8	V.S.	R.I.	V.S.	R.I.	S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Setacyl Navy Blue CGN (Gy)	—	S.	R.I.	S.	R.I.	S.	R.I.	S.	R.I.	M.S.	R.I.	M.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Cibacet Blue Green EB (Ciba)	—	V.S.	R.I.	V.S.	R.I.	S.	R.I.	M.S.	R.I.	S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.
Multamine Brilliant Green B (ICI)	—	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Serinyl Hosiery Brown GN (YDC)	—	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.
DYEING TEMPERATURE 60°C.																	
Setacyl Orange RE	C.I. Disperse Orange 3	M.S.	R.I.	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.	V.S.	R.I.	S.	R.I.	M.S.	R.I.	S.	R.I.
Cibacet Red E3B	C.I. Disperse Red 15	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.
Serisol Fast Violet RGL (YDC)	—	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.
Duranol Brilliant Blue BN	C.I. Disperse Blue 3	S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Artisil Brown NR (S)	—	S.	R.I.	V.S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.	S.	R.I.	S.	R.I.	V.S.	R.I.
Multamine Grey B (ICI)	—	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.

TABLE XIV

Effects of Time and Temperature on the Covering Properties of Disperse Dyes

Dye (2%)	*Colour Index* No.	85°c. for 1 hr.		85°c. for 2 hr.		85°c. for 4 hr.		100°c. for 1 hr.		100°c. for 2 hr.	
		Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.	Phys.	Chem.
Dispersol Fast Orange Brown R ...	C.I. Disperse Orange 5	S.	R.I.	S.	R.I.	S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Scarlet GFL	C.I. Disperse Red 43	V.S.	R.I.	S.	R.I.	S.	R.I.	S.	R.I.	S.	R.I.
Artisil Red BP	C.I. Disperse Red 24	V.S.	R.I.	S.	R.I.	S.	R.I.	M.S.	R.I.	S.S.	R.I.
Cibacet Red BBS	C.I. Disperse Red 24	V.S.	R.I.	V.S.	R.I.	S.	R.I.	S.S.	R.I.	S.S.	R.I.
Multamine Brilliant Green B (ICI) ...	—	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.

the ability of the disperse dyes to cover physical variations in general increases. A marked difference between 60°C. and 85°C. dyeings is often observed, although with some dyes there is little improvement until 100°C. is reached (cf. Tables XI and XII).

EFFECT OF DISPERSING AGENTS—A factor which might affect the levelling properties of disperse dyes is the dispersing agent used in the dyebath. In order to avoid complications, the initial series were all dyed in the presence of 1 c.c. of Dispersol VL (ICI) per litre. Subsequently a number of those dyes which were sensitive under these conditions were dyed to a 2% depth at 85°C. using dispersing agents recommended by various dye manufacturers.

From the results in Table XIII, it can be seen that, with one exception, the change of dispersing agent has had little effect on the covering property of the dye, a maximum difference of one point being observed.

A smaller selected range of dyes was also dyed at 60°C. using the same series of dispersing agents. Some slight variations between agents were observed (Table XIII), but there was no definite trend to indicate that one class of agent shows a significant improvement over another.

In general, improvement in coverage can be obtained by increase in temperature. Experiments were also made to determine whether an increase in time of dyeing within practical limits would achieve the same results. Little further improvement over dyeing for one hour was obtained by prolonging the dyeing time (Table XIV). All the available evidence points to one factor to promote coverage—as high a dyeing temperature as possible.

As an extension to this laboratory work, a trial was made. A tightly woven highly rated fabric which was known to be prone to warp stripiness was divided into three parts and dyed with Duranol Blue Green B (C.I. Disperse Blue 7) as follows—

(i) In an open jig
(ii) In an enclosed jig
(iii) In a pressure jig at 25 lb./sq.in.

The difference in coverage was as expected, the open jig being worst and the pressure jig best.

The most interesting point, however, was the marked improvement in coverage on the enclosed jig compared with the open jig. There are only a limited number of pressure jigs in the trade, and these expensive machines are used more for the dyeing of the newer synthetic fibres than for nylon, to which it is comparatively easy to apply colour. Provided that nylon is dyed as near the boil as possible, improved results will be obtained. This, in conjunction with dye selection, will reduce overall stripiness to a minimum.

However, although there are available in the trade large numbers of enclosed jigs and winches, antipathy towards their correct use exists. Many reasons for leaving the machines open are advanced. The chief one appears to be the plea that it is extremely difficult for the operator adequately to supervise several machines when the lids are down and his vision is obstructed. This difficulty is not insuperable, since it is overcome in the dyeing of polyester and acrylic fibres above 100°C. Although it is relatively simple to apply disperse dyes to nylon fabrics, improved results will be obtained both by keeping the temperature as high as possible, and by dye selection. Where it is not practicable to dye all fabrics at temperatures near the boil, then fabric selection can be made. Dyers can usually tell which type of fabrics are liable to give trouble from stripiness. These materials should then be dyed in the enclosed machines.

8. DISCUSSION AND CONCLUSIONS

The problem facing the dyer of continuous-filament nylon fabrics is to dye them uniformly to a colour whose fastness characteristics are adequate for the proposed end-use. As explained in the introduction, these two requirements are not always compatible, and we now have to consider to what extent the work described in this paper can bridge the gap between them.

The variations in nylon yarn are known to be of two main types, viz., in physical structure and in amine end-group content. Because it is possible for the yarn producer to measure and control amine end-group content, physical structure irregularity within and between nylon yarns represents the major cause of dyeing irregularity. As a means of minimising this variation, the appended sensitivity lists will be valuable, since among the dyes listed are many whose sensitivities to physical structure variations in nylon are of a low order. It must be emphasised, however, that use of such dyes is not a guarantee of fault-free dyeings: we should prefer to regard these lists as guides to the dyer, rather than as rules. Low sensitivity to physical variations is not a property of any single class of dye: such dyes can be found among acid wool dyes, azoic dyes, soluble dyes for cellulose acetate, and the afterchrome dyes, but one class of dyes is less suitable for application to filament nylon by normal methods (except in heavy depths). These, unfortunately, are the neutral-dyeing metal-complex dyes, which are all extremely sensitive to structural differences in nylon. The word "unfortunately" is used, since these dyes exhibit many desirable properties on nylon, their fastness to light and to wet treatments being high, and their building-up properties excellent. Where any stripiness and barriness will be so apparent as to make a fabric or garment unacceptable, and where conventional dyeing methods are to be employed, these dyes cannot safely be used.

It is thus fortunate that, although many of the more suitable acid dyes have lower wet fastness than have the metal-complex dyes, a simple after-treatment is capable of producing a considerable improvement in this property. This is generally referred to as *back-tanning* [16], and is applicable to the majority of water-soluble dyes. Little or no change in colour is produced, and light fastness is similarly unaffected. Use of selected acid dyes followed by back-tanning is a valuable approach to the combining of uniformity with fastness.

Where acid wool dyes are unsatisfactory, perhaps because of incompatibility in admixture, then use of the soluble dyes for cellulose acetate may be helpful. These are more sensitive to yarn variations than are disperse dyes, but as a range are no more sensitive than are the majority of acid wool dyes, and their wet fastness is also markedly improved by back-tanning.

For certain colours selected azoic combinations, and prepared mixtures of diazo and coupling components are capable of affording good coverage of variations, with considerable improvement in wet fastness over disperse dyes— this is particularly true when heavy depths of, say, maroon are required. At their best, azoic dyes are capable of covering irregularities at least as well as the great majority of disperse dyes.

A few afterchrome dyes are worthy of consideration. The main value of this class of dye will probably still be in heavy depths (niggers, blacks, navy blues), where high wash fastness is essential and in which variations will be less easily seen.

There will, of course, always be instances in which disperse dyes will be used, and it is important to note that there is a considerable variation among these dyes in sensitivity to the physical structure of nylon. Some care is therefore necessary in selecting suitable disperse dyes, particularly where only open machinery is available. This last point is emphasised, since, of all the dye types examined, disperse dyes are more affected by temperature in their behaviour towards physical structure variations than are any of the other classes.

It is well established that dyeing technique can influence, adversely or otherwise, the quality of a dyeing, by its effect on such dye properties as levelling and migrating power. It is also true that coverage of physical structure variations in nylon yarns is subject to dyeing conditions, and that attention to a few relatively simple points may do much to ensure commercial acceptability. As high a dyeing temperature as possible should be maintained. In practice this means that enclosed machinery must be used where it is available, and in particular that enclosed jigs should be operated as enclosed jigs. The effective dyeing temperature on the rolls of an open jig is much lower than that of the bath itself, and where undue stripiness is encountered with disperse dyes applied on an open jig, dyeing under enclosed conditions will bring about considerable improvement. This may mean the difference between commercial acceptability and rejection. Level-dyeing acid wool dyes are affected similarly, but less success is experienced with dyes which do not migrate as easily. Theoretically, it would be possible to ensure greater uniformity by starting dyeing at a high temperature, but this would have to be combined with the use of a retarding agent to prevent too rapid an initial absorption of dye by the fibre. As high a dyeing temperature as possible is also advantageous for good penetration and reduction of dyeing times, and the gains from operating enclosed machinery would seem to outweigh any difficulties such as inspection of fabric during dyeing.

The foregoing paragraph has been concerned with temperatures up to 100°C., and the effects of temperatures in the range 100–130°C. may be regarded as an extension of this work. Disperse dyes continue to show improvement in coverage in this range, and it may be necessary to use these conditions with certain of the more poorly covering members. Level-dyeing acid wool dyes also show some improvement, and, as their wet fastness can be made considerably better by back-tanning, this method may well be of value for colours in the pale to medium range. Metal-complex dyes have, in the present work, shown no appreciable improvement in coverage at these temperatures. Thus dyeing at high temperature, although by no means the complete answer to the problem, has a valuable contribution to make in minimising dyeing irregularity, particularly with disperse dyes.

None of the work with swelling, restraining, and retarding agents has yielded results which are of immediate value. Although slightly better coverage has been obtained in some instances, it has not yet justified the making of firm recommendations. However, this is by no means to imply that such approaches to the problem are worthless, since more detailed investigations are clearly desirable, both to confirm or deny present results and to break new ground.

The most promising techniques for the application of "fast" dyes to woven fabric are probably those based on a preliminary padding of the cloth with dye solution, followed by a fixation stage. As indicated in § 5, important points are the avoidance of affinity effects during padding and of migration of dye during fixation. In contrast to conventional dyeing techniques, these procedures may favour the use of neutral-dyeing metal-complex dyes, since these show little tendency to migrate and level in a normal dyeing, and should therefore be capable of fixation to the fabric without migration occurring. More thorough investigation of fixation techniques is necessary to establish optimum conditions, and a considerable amount of work is needed on padding conditions, e.g. on composition and temperature of padding liquor, dye solubility under various conditions, etc. These considerations apart, the principle of pad–fixation methods has been demonstrated to be of value in minimising stripes and barriness, and of all current approaches this is probably the most promising. There may be a restriction in that heavier dyeings may not be so successful as pale and medium, but incorporation of swelling agents in the pad liquor [13] may help to overcome this.

Pigment–resin dispersion padding followed by a curing stage will probably prove to be of value, particularly in pale to medium depths. Some restriction may be imposed on heavier depths by diminished rubbing fastness.

Another line of investigation, which might prove fruitful, but which lies outside the scope of this paper, is the production of new dye types for nylon. As yet no new dye class has been introduced specifically for nylon, this being a natural consequence of its affinity for most of the existing

ranges. However, the more complete understanding of the nature of the problem of dyeing irregularity does increase the desirability of dyes similar in their dyeing characteristics to disperse dyes, but possessing higher fastness. Whether this is a practical proposition or not is for the dye manufacturer to decide, but, at least on paper, the idea of a disperse dye which could be applied as such, and subsequently metallised, is attractive.

Fabric designers and manufacturers can also make positive contributions towards the reduction of apparent stripiness and barriness. The designer must be aware of the limitations attached to the dyeing of nylon, so that, as an imaginary example, there will be no danger of his designing a warp-faced satin from continuous-filament nylon, whose end-use requires that metal-complex dyes be used. The effects of patterns in breaking up any stripiness in a ground colour are pronounced, a twill weave being better than a plain weave. A simple motif repeated on the fabric is often sufficient to distract the observer's eye from imperfections in the ground. This is now of known value for printed nylon fabrics, in that a fast-dyed ground, although perhaps stripy, does not appear objectionably so when overprinted.

There is, then, still much for all concerned with continuous-filament nylon to do. From yarn producer to finisher, all have valuable contributions to make, which will be reflected in the quality and the appearance of the finished product, and there are still many aspects of dyeing technique alone which deserve much fuller investigation than we have been able to give. However, we feel that this paper will have fulfilled its purpose if it has made the nature of the problems clearer, and if it serves both as a practical guide to the dyer and as a stimulus to further investigations.

Appendix

DYE SENSITIVITIES TO PHYSICAL AND CHEMICAL VARIATIONS IN NYLON

The following tables contain ratings, made visually by comparison with a set of control dyeings, of the sensitivities of a large number of dyes, considered to be of practical interest, towards the physical structure and chemical variations contained in the experimental fabric. The tables are divided into two main sections— (i) dyes other than disperse dyes (i.e. acid, direct, chrome, metal-complex, and azoic dyes) and (ii) disperse dyes. Each section is subdivided under manufacturers' names. Except where otherwise indicated, all dyeings have been made in 2% depth.

DYES OTHER THAN DISPERSE DYES

Badische Anilin- und Soda-Fabrik AG.

Dye [1]	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
	METAL-COMPLEX DYES		
Vialon Fast Yellow R	C.I. Acid Yellow 119	V.S.	S.S.
Vialon Fast Yellow G	C.I. Acid Yellow 118	V.S.	S.S.
Vialon Fast Orange R	C.I. Acid Orange 89	V.S.	M.S.
Vialon Fast Red G	C.I. Acid Red 226	V.S.	M.S.
Vialon Fast Red B	C.I. Acid Red 225	V.S.	S.S.
Vialon Fast Bordeaux R	—	V.S.	R.I.
Vialon Fast Violet B	C.I. Acid Violet 74	V.S.	M.S.
Vialon Fast Blue KFM	—	V.S.	S.S.
Vialon Fast Blue Grey B	C.I. Acid Black 61	V.S.	M.S.
Vialon Fast Green FFG	C.I. Acid Green 46	V.S.	M.S.
Vialon Fast Olive B	—	V.S.	M.S.
Vialon Fast Brown R	C.I. Acid Brown 50	V.S.	S.S.–M.S.
Vialon Fast Brown GR	—	V.S.	S.S.
Vialon Fast Copper Brown R	—	V.S.	R.I.
Vialon Fast Navy Blue R	—	V.S.	S.S.
Vialon Fast Black G (5%)	—	V.S.	M.S.
Vialon Fast Black G (10%)	—	S.	S.S.
Vialon Fast Black R (5%)	C.I. Acid Black 63	V.S.	S.S.
Vialon Fast Black R (10%)	C.I. Acid Black 63	R.I.	S.S.
Ortolan Yellow G	C.I. Acid Yellow 59	V.S.	S.
Ortolan Orange R	C.I. Acid Orange 39	V.S.	R.I.
Ortolan Red G	C.I. Acid Red 221	V.S.	S.S.
Ortolan Brown GR	—	V.S.	M.S.
Ortolan Brown 3R	C.I. Acid Brown 33	V.S.	S.
Ortolan Violet B	C.I. Acid Violet 46	V.S.	S.S.
Ortolan Blue G	C.I. Acid Blue 151	V.S.	R.I.
Ortolan Black G Special	—	V.S.	R.I.
Ortolan Black G Special (5%)	—	V.S.	S.S.
Ortolan Black G Special (10%)	—	V.S.	R.I.

Dye	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
Brotherton & Co. Ltd.			
CHROME DYES			
Chrome Yellow MY (3%)	C.I. Mordant Yellow 12	S.	V.S.
Metachrome Orange R (3%)	C.I. Mordant Orange 1	R.I.	V.S.
Metachrome Red 5G (3%)	C.I. Mordant Red 19	S.S.	V.S.
Metachrome Violet 6R (3%)	C.I. Mordant Violet 9	S.	S.
Unachrome Navy Blue 2R (4%)	C.I. Mordant Blue 9	M.S.	V.S.
Metachrome Blue Black 2BX (4%)	C.I. Mordant Black 29	M.S.	V.S.
Ciba Ltd. and The Clayton Dyestuffs Co. Ltd.			
ACID DYES			
Kiton Yellow 7GF	C.I. Acid Yellow 3	M.S.	S.
Kiton Yellow S	C.I. Acid Yellow 27	R.I.	S.S.
Kiton Yellow T	C.I. Acid Yellow 23	S.S.	V.S.
Kiton Orange MNO	C.I. Acid Yellow 36	S.S.	V.S.
Kiton Orange II	C.I. Acid Orange 7	R.I.	V.S.
Kiton Ponceau 3G	—	S.S.	V.S.
Kiton Ponceau R	C.I. Acid Red 26	S.S.	V.S.
Kiton Scarlet R	C.I. Acid Red 102	S.S.	V.S.
Kiton Red S	C.I. Acid Red 7	M.S.	V.S.
Kiton Crimson 2R	C.I. Acid Red 14	S.S.	V.S.
Kiton Rhodamine B	C.I. Acid Red 52	V.S.	V.S.
Kiton Fuchsine A2R	C.I. Acid Violet 9	S.	V.S.
Kiton Green A	C.I. Acid Green 7	V.S.	V.S.
Kiton Green B	C.I. Acid Green 9	S.	V.S.
Kiton Fast Yellow 2GL	C.I. Acid Yellow 17	R.I.	S.
Kiton Fast Yellow G	C.I. Acid Yellow 29	S.S.–M.S.	V.S.
Kiton Fast Yellow 2GRL	C.I. Acid Yellow 29	S.S.	S.
Kiton Fast Yellow A	C.I. Acid Orange 3	S.S.	V.S.
Kiton Fast Scarlet A	C.I. Acid Red 73	S.S.	V.S.
Kiton Fast Red R	C.I. Acid Red 5	S.S.	S.
Kiton Fast Red 3GP	—	S.	V.S.
Kiton Fast Red G	C.I. Acid Red 1	R.I.	V.S.
Kiton Fast Red 4BLN	C.I. Acid Violet 14	S.	V.S.
Kiton Fast Rubine GRL	C.I. Acid Red 58	M.S.	V.S.
Kiton Fast Rubine 4BL	C.I. Acid Violet 26	M.S.	V.S.
Kiton Fast Violet R	C.I. Acid Violet 43	S.S.	V.S.
Kiton Fast Blue 4GL	C.I. Acid Blue 23	S.	V.S.
Kiton Fast Blue 2GR	C.I. Acid Blue 50	S.	V.S.
Kiton Fast Blue GS	C.I. Acid Blue 55	S.	V.S.
Kiton Fast Blue G	C.I. Acid Blue 43	S.S.	V.S.
Kiton Fast Blue CR	C.I. Acid Blue 47	M.S.	V.S.
Kiton Fast Blue GRC	—	S.	V.S.
Alizarine Fast Fuchsine RL	—	S.	V.S.
Alizarine Fast Violet 6R	C.I. Acid Violet 31	V.S.	V.S.
Alizarine Fast Violet RBF	C.I. Acid Violet 33	S.S.	V.S.
Alizarine Fast Violet 2RL	Similar to C.I. Acid Violet 36	S.S.	V.S.
Alizarine Fast Violet FRL	C.I. Acid Violet 48	V.S.	V.S.
Alizarine Fast Blue BE	C.I. Acid Blue 129	S.	V.S.
Alizarine Fast Blue 3GE	C.I. Acid Blue 106	S.	V.S.
Alizarine Fast Blue R	C.I. Acid Blue 80	S.	V.S.
Alizarine Fast Green G	C.I. Acid Green 25	V.S.	V.S.
Alizarine Fast Green 2GW	C.I. Acid Green 40	V.S.	V.S.
Alizarine Fast Grey G	C.I. Acid Black 50	M.S.	V.S.
Alizarine Fast Grey BLL	Similar to C.I. Acid Black 48	S.	V.S.
Benzyl Yellow 5G	—	R.I.	R.I.
Benzyl Orange 2R	C.I. Acid Orange 45	M.S.	V.S.
Benzyl Scarlet BS	—	S.S.	V.S.
Benzyl Scarlet 3BS	—	S.S.	V.S.
Benzyl Red GR	C.I. Acid Red 85	S.S.	S.
Benzyl Red R	C.I. Acid Red 123	S.	S.
Benzyl Red 2BG	—	M.S.	S.
Benzyl Red A	C.I. Acid Red 141	S.S.	V.S.
Benzyl Red S	C.I. Acid Red 88	S.S.	V.S.
Benzyl Red MG	C.I. Acid Red 97	S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
Benzyl Red MR	C.I. Acid Red 89	M.S.	V.S.
Benzyl Blue 3GL	Similar to C.I. Acid Blue 61	V.S.	V.S.
Benzyl Blue GL	C.I. Acid Blue 102	V.S.	V.S.
Benzyl Blue BL	C.I. Acid Blue 59	S.	V.S.
Benzyl Cyanine 6B	C.I. Acid Blue 83	V.S.	V.S.
Benzyl Cyanine EG	—	V.S.	V.S.
Benzyl Green 2BW	C.I. Acid Green 19	S.	V.S.
Benzyl Fast Yellow GR	C.I. Acid Yellow 40	R.I.	M.S.
Benzyl Fast Yellow RS	C.I. Acid Yellow 42	S.	V.S.
Benzyl Fast Yellow 2RN	C.I. Acid Yellow 65	S.	M.S.
Benzyl Fast Orange G	C.I. Acid Orange 47	S.	S.
Benzyl Fast Brown NR	C.I. Acid Orange 51	S.	S.
Benzyl Fast Scarlet G	—	S.S.	V.S.
Benzyl Fast Red BG	C.I. Acid Red 99	M.S.	V.S.
Benzyl Fast Red 3BG	C.I. Acid Red 167	S.	V.S.
Benzyl Fast Red 2G	C.I. Acid Red 111	M.S.	V.S.
Benzyl Fast Red 3G	C.I. Acid Red 104	S.S.	S.S.
Benzyl Fast Red B	C.I. Acid Red 106	S.S.	V.S.
Benzyl Fast Red 2B	C.I. Acid Red 115	S.S.	S.
Benzyl Fast Red 10B	C.I. Acid Violet 5	S.	V.S.
Benzyl Fast Rubine 2B	C.I. Acid Red 133	M.S.	V.S.
Benzyl Fast Rubine 3BW	C.I. Acid Red 129	S.	V.S.
Benzyl Fast Rubine 4BN	C.I. Acid Red 131	S.	V.S.
Benzyl Fast Rubine 8B	—	S.	V.S.
Benzyl Fast Bordeaux 2B	C.I. Acid Red 120	V.S.	V.S.
Benzyl Fast Black B	C.I. Acid Black 24	V.S.	V.S.
Benzyl Fast Black B (5%)	C.I. Acid Black 24	M.S.	V.S.
Benzyl Fast Black B (10%)	C.I. Acid Black 24	S.S.	S.S.
Benzyl Fast Black 3B	C.I. Acid Black 24	S.	V.S.
Benzyl Fast Black 3B (5%)	C.I. Acid Black 24	M.S.	S.
Benzyl Fast Black 3B (10%)	C.I. Acid Black 24	S.S.	M.S.
Benzyl Fast Black BX	—	S.	V.S.
Benzyl Fast Black BX (5%)	—	S.S.	S.
Benzyl Fast Black BX (10%)	—	S.S.	S.S.
Benzyl Fast Black 4BN	C.I. Acid Black 26A	V.S.	V.S.
Benzyl Fast Black 4BN (5%)	C.I. Acid Black 26A	M.S.	V.S.
Benzyl Fast Black 4BN (10%)	C.I. Acid Black 26A	S.S.	V.S.
Cloth Fast Blue RN	C.I. Acid Blue 113	S.	V.S.
Cloth Fast Blue GTB	C.I. Acid Blue 118	M.S.	V.S.
	CHROME DYES		
Chrome Fast Flavine A	C.I. Mordant Yellow 5	S.	V.S.
Chrome Fast Yellow G	C.I. Mordant Yellow 16	R.I.	M.S.
Chrome Fast Orange G	C.I. Mordant Orange 6	R.I.	S.
Chrome Fast Orange R	C.I. Mordant Orange 10	S.S.	V.S.
Chrome Fast Orange 2RL	C.I. Mordant Orange 5	S.	V.S.
Chrome Fast Brown EBC	C.I. Mordant Brown 1	M.S.	V.S.
Chrome Fast Brown TV	C.I. Mordant Brown 33	S.S.	V.S.
Chrome Fast Brown DKL	C.I. Mordant Brown 19	V.S.	V.S.
Chrome Fast Brown V	C.I. Mordant Brown 35	S.S.	V.S.
Chrome Fast Brown R	C.I. Mordant Brown 29	V.S.	V.S.
Chrome Fast Brown 2R	C.I. Mordant Brown 57	S.	V.S.
Chrome Fast Brown P	C.I. Mordant Brown 31	M.S.	V.S.
Metachrome Brown G	C.I. Mordant Brown 5	S.	V.S.
Metachrome Brown R	C.I. Mordant Brown 4	S.	V.S.
Metachrome Brown BR	C.I. Mordant Brown 12	S.	V.S.
Metachrome Brown 6G	C.I. Mordant Brown 24	V.S.	S.
Metachrome Olive Brown G	C.I. Mordant Brown 6	S.	V.S.
Chrome Fast Red 2B	C.I. Mordant Red 7	R.I.	V.S.
Chrome Fast Red G	C.I. Mordant Red 17	S.	V.S.
Chrome Fast Red 2G	C.I. Mordant Red 19	M.S.	V.S.
Synchromate Red GR	C.I. Mordant Red 40	M.S.	V.S.
Naphthochrome Violet R	C.I. Mordant Violet 3	S.	V.S.
Naphthochrome Violet RB	—	M.S.	V.S.
Naphthochrome Violet 2B	C.I. Mordant Violet 28	S.	V.S.
Naphthochrome Azurine B	C.I. Mordant Blue 28	M.S.	V.S.
Naphthochrome Azurine 2B	C.I. Mordant Blue 1	S.S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
Chrome Fast Cyanine 2BSS	C.I. Mordant Blue 5	S.	V.S.
Chrome Fast Cyanine BSS	C.I. Mordant Blue 5	V.S.	V.S.
Chrome Fast Cyanine B	—	S.	V.S.
Chrome Fast Cyanine BN	C.I. Mordant Black 17	S.	V.S.
Chrome Fast Cyanine GP	C.I. Mordant Blue 11	V.S.	S.
Chrome Fast Cyanine GNN	C.I. Mordant Blue 11	S.	V.S.
Chrome Fast Cyanine GN	C.I. Mordant Blue 11	V.S.	V.S.
Chrome Fast Cyanine G	C.I. Mordant Blue 11	S.	V.S.
Synchromate Blue 2RB	C.I. Mordant Blue 30	M.S.	V.S.
Synchromate Blue B2G	C.I. Mordant Blue 41	M.S.	V.S.
Naphthochrome Green G	C.I. Mordant Green 31	V.S.	V.S.
Chrome Fast Green FG	C.I. Mordant Green 18	V.S.	V.S.
Alizarine Fast Green G	C.I. Acid Green 25	V.S.	V.S.
Alizarine Fast Green 2GW	C.I. Acid Green 40	V.S.	V.S.
Chrome Fast Olive GL	C.I. Mordant Green 35	S.	V.S.
Alizarine Blue Black B	C.I. Mordant Black 13	M.S.	V.S.
Alizarine Blue Black B (5%)	C.I. Mordant Black 13	M.S.	V.S.
Alizarine Blue Black B (10%)	C.I. Mordant Black 13	M.S.	V.S.
Chrome Fast Grey GL	C.I. Mordant Black 38	M.S.	V.S.
Chrome Fast Black CAT	C.I. Mordant Black 11	V.S.	V.S.
Chrome Fast Black CAT (5%)	C.I. Mordant Black 11	S.S.	S.
Chrome Fast Black CAT (10%)	C.I. Mordant Black 11	R.I.	M.S.
Chrome Fast Black K1T	C.I. Mordant Black 11	V.S.	V.S.
Chrome Fast Black K1T (5%)	C.I. Mordant Black 11	S.	V.S.
Chrome Fast Black K1T (10%)	C.I. Mordant Black 11	M.S.	V.S.
Chrome Fast Black A	C.I. Mordant Black 1	V.S.	V.S.
Chrome Fast Black A (5%)	C.I. Mordant Black 1	S.S.	V.S.
Chrome Fast Black A (10%)	C.I. Mordant Black 1	S.S.	S.
Chrome Fast Black FW	C.I. Mordant Black 5	S.	V.S.
Chrome Fast Black FW (5%)	C.I. Mordant Black 5	S.S.	V.S.
Chrome Fast Black FW (10%)	C.I. Mordant Black 5	S.S.	M.S.
Chrome Fast Black FBW	C.I. Mordant Black 5	S.	V.S.
Chrome Fast Black FBW (5%)	C.I. Mordant Black 5	S.S.	V.S.
Chrome Fast Black FBW (10%)	C.I. Mordant Black 5	S.S.	M.S.
	METAL-COMPLEX DYES		
Neolan Flavine GFE	C.I. Acid Yellow 103	S.S.	V.S.
Neolan Yellow GR	C.I. Acid Yellow 99	S.	V.S.
Neolan Orange G	C.I. Acid Orange 74	V.S.	S.
Neolan Violet Brown B	C.I. Acid Red 184	V.S.	V.S.
Neolan Red REG	C.I. Acid Red 198	S.	V.S.
Neolan Red GRE	C.I. Acid Red 183	V.S.	V.S.
Neolan Pink BA	C.I. Acid Red 186	V.S.	V.S.
Neolan Pink BE	C.I. Acid Red 195	V.S.	V.S.
Neolan Bordeaux RM	C.I. Acid Red 194	V.S.	S.
Neolan Violet 5RF	C.I. Acid Violet 58	V.S.	V.S.
Neolan Violet RM	—	V.S.	V.S.
Neolan Blue 2G	C.I. Acid Blue 158A	V.S.	V.S.
Neolan Blue 2R	C.I. Acid Blue 154	V.S.	V.S.
Neolan Green BL conc.	C.I. Acid Green 12	S.	V.S.
Neolan Green BF	C.I. Acid Green 12	S.	V.S.
Neolan Green B	C.I. Acid Green 12	V.S.	V.S.
Neolan Green BG	—	V.S.	V.S.
Neolan Green 8G	C.I. Acid Green 24	V.S.	V.S.
Neolan Dark Green B	C.I. Acid Green 35	V.S.	V.S.
Neolan Grey 3B	C.I. Acid Black 51	V.S.	V.S.
Neolan Black 2G	C.I. Acid Black 54	V.S.	V.S.
Neolan Black 2G (5%)	C.I. Acid Black 54	V.S.	V.S.
Neolan Black 2G (10%)	C.I. Acid Black 54	V.S.	V.S.
Neolan Black 2R	C.I. Acid Black 43	S.	V.S.
Neolan Black 2R (5%)	C.I. Acid Black 43	S.	V.S.
Neolan Black 2R (10%)	C.I. Acid Black 43	M.S.	V.S.
Neolan Black WA Extra	C.I. Acid Black 52	V.S.	V.S.
Neolan Black WA Extra (5%)	C.I. Acid Black 52	S.	V.S.
Neolan Black WA Extra (10%)	C.I. Acid Black 52	M.S.	S.
Cibalan Brilliant Yellow 3GL	—	S.	S.
Cibalan Yellow FGL	—	V.S.	S.S.
Cibalan Yellow GRL	C.I. Acid Yellow 116	V.S.	S.S.
Cibalan Yellow 2BRL	C.I. Acid Orange 87	V.S.	S.S.
Cibalan Orange RL	C.I. Acid Orange 88	V.S.	S.S.

Dye	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
Cibalan Khaki GL	—	V.S.	S.S.
Cibalan Brown 5RL	—	V.S.	S.S.
Cibalan Brown TL	C.I. Acid Brown 21	V.S.	S.
Cibalan Brown VRL	—	V.S.	S.S.
Cibalan Brown BL	C.I. Acid Brown 19	V.S.	S.
Cibalan Brown 2GL	—	V.S.	M.S.
Cibalan Scarlet GL	C.I. Acid Red 209	V.S.	R.I.
Cibalan Red 2GL	C.I. Acid Red 211	V.S.	S.S.
Cibalan Brilliant Red BL	—	V.S.	S.S.
Cibalan Bordeaux RL	C.I. Acid Violet 71	V.S.	R.I.
Cibalan Bordeaux GRL	C.I. Acid Red 213	V.S.	S.S.
Cibalan Bordeaux 3BL	C.I. Acid Violet 70	V.S.	R.I.
Cibalan Corinth BL	—	V.S.	S.S.
Cibalan Violet RL	C.I. Acid Violet 68	V.S.	S.S.
Cibalan Blue FBL	—	V.S.	S.S.
Cibalan Blue BRL	C.I. Acid Blue 170	V.S.	R.I.
Cibalan Blue BL	C.I. Acid Blue 168	V.S.	S.S.
Cibalan Blue 3GL	C.I. Acid Blue 171	V.S.	R.I.
Cibalan Brilliant Blue GL	—	V.S.	V.S.
Cibalan Green GL	C.I. Acid Green 43	V.S.	S.S.
Cibalan Grey BL	C.I. Acid Black 60	V.S.	M.S.
Cibalan Grey 2GL	C.I. Acid Black 60	V.S.	S.S.
Cibalan Black BGL	—	V.S.	S.
Cibalan Black BGL (5%)	—	V.S.	M.S.
Cibalan Black BGL (10%)	—	S.	S.S.
ELANYL DYES			
Elanyl Yellow G	—	S.	S.S.
Elanyl Orange R	—	V.S.	S.S.
Elanyl Scarlet G	—	V.S.	S.
Elanyl Red B	—	V.S.	S.S.
Elanyl Bordeaux B	—	V.S.	S.S.
Elanyl Blue 2G	—	M.S.	V.S.
Elanyl Navy Blue G	—	V.S.	V.S.
Elanyl Dark Green B	—	V.S.	S.S.
Elanyl Green 2G	—	M.S.	V.S.
Elanyl Brown 2R	—	V.S.	M.S.
Elanyl Grey G	—	V.S.	S.S.
Farbwerke Hoechst AG.			
INTRAMINE DYES			
Intramine Orange R	—	S.S.	R.I.
Intramine Red B	—	M.S.	R.I.
Intramine Bordeaux B	—	M.S.	R.I.
Intramine Khaki G	—	S.	S.
Intramine Brown RB	—	S.	S.
Intramine Brown GG	—	S.	S.
Intramine Brown GR	—	M.S.	S.
Intramine Navy Blue R (3%)	—	S.S.	R.I.
Intramine Black B (5%)	—	S.S.	R.I.
AZOIC COMBINATIONS			
g./litre			
4·0 Ofna-perl Salt SBR	—		
1·0 Naphtol AS–GD	—	M.S.	R.I.
1·5 Ofna-perl Salt SBR	—		
0·5 Naphtol AS–SG	C.I. Azoic Coupling Component 13	S.S.	R.I.
4·0 Ofna-perl Salt SBR	—		
0·8 Naphtol AS–GP	C.I. Azoic Coupling		
0·4 Naphtol AS–RP	Components 38 and 39	M.S.	S.
3·0 Ofna-perl Salt SBR	—		
1·0 Naphtol AS–RP	C.I. Azoic Coupling Component 39	S.S.	M.S.
1·5 Ofna-perl Salt SBR	—		
0·5 Naphtol AS–SG	C.I. Azoic Coupling		
0·1 Naphtol AS–GP	Components 13 and 38	S.S.	S.S.
7·0 Ofna-perl Salt SBR	—		
2·0 Naphtol AS–GP	C.I. Azoic Coupling Component 38	M.S.	S.–V.S.
6·0 Ofna-perl Salt SBR	—		
2·0 Naphtol AS–RP	C.I. Azoic Coupling Component 39	S.S.	S.
3·5 Ofna-perl Salt SBR	—		
1·0 Naphtol AS–GP	C.I. Azoic Coupling Component 38	M.S.	V.S.

Dye g./litre	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
3·5 Ofna-perl Salt SBR	—		
0·9 Naphtol AS–RD	—		
0·1 Naphtol AS–SG	C.I. Azoic Coupling Component 13	S.S.	S.S.
3·5 Ofna-perl Salt SBR	—		
0·9 Naphtol AS–GP	C.I. Azoic Coupling		
0·1 Naphtol AS–SG	Components 38 and 13	S.S.	R.I.
0·5 Ofna-perl Salt SBR	—		
0·5 Naphtol AS–LB	C.I. Azoic Coupling Component 15	S.S.	R.I.
0·5 Ofna-perl Salt SBR	—		
0·2 Naphtol AS–SG	C.I. Azoic Coupling Component 13	V.S.	S.S.
0·5 Ofna-perl Salt SBR	—		
1·0 Naphtol AS–L3G	C.I. Azoic Coupling Component 33	S.	R.I.
0·5 Ofna-perl Salt RRA	—		
1·0 Naphtol AS–L3G	C.I. Azoic Coupling Component 33	M.S.	R.I.
0·5 Ofna-perl Salt RRA	—		
0·5 Naphtol AS–LB	C.I. Azoic Coupling Component 15	S.S.	R.I.
0·5 Ofna-perl Salt RRA	—		
0·5 Naphtol AS–SR	C.I. Azoic Coupling Component 25	M.S.	V.S.
0·5 Ofna-perl Salt RRA	—		
0·2 Naphtol AS–SG	C.I. Azoic Coupling Component 13	M.S.	V.S.
0·5 Ofna-perl Salt BBA	—		
0·5 Naphtol AS–SR	C.I. Azoic Coupling Component 25	V.S.	S.
0·5 Ofna-perl Salt BBA	—		
0·2 Naphtol AS–SG	C.I. Azoic Coupling Component 13	S.	S.S.
0·5 Ofna-perl Salt BBA	—		
1·0 Naphtol AS–L3G	C.I. Azoic Coupling Component 33	V.S.	R.I.
0·5 Ofna-perl Salt BBA	—		
0·5 Naphtol AS–LB	C.I. Azoic Coupling Component 15	V.S.	R.I.
	The Geigy Co. Ltd.		
	ACID DYES		
Erio Flavine SX	C.I. Acid Yellow 17	R.I.	S.
Erio Fast Floxine BL	C.I. Acid Red 37	S.S.	V.S.
Erio Anthracene Rubine 2BF	—	V.S.	V.S.
Acid Red XB	C.I. Acid Red 52	V.S.	S.
Erio Anthracene Cyanine RL	C.I. Acid Violet 33	M.S.	V.S.
Erio Anthracene Blue R	C.I. Acid Blue 47	M.S.	V.S.
Erio Fast Yellow 4GS	—	S.S.	V.S.
Erio Fast Yellow GLS	C.I. Acid Yellow 19	S.S.	S.
Erio Fast Yellow RS	C.I. Acid Yellow 25	S.S.	S.
Erio Fast Red 2GS	C.I. Acid Orange 19	S.S.	V.S.
Erio Fast Red G	C.I. Acid Red 75	S.S.	V.S.
Erio Fast Red 2BLS	C.I. Acid Red 42	S.	V.S.
Erio Fast Brown R	C.I. Acid Brown 2	S.	V.S.
Erio Anthracene Brilliant Blue BFF	C.I. Acid Blue 129	S.	V.S.
Erio Anthracene Brilliant Blue F3GL	—	S.	V.S.
Erio Fast Cyanine Green G	C.I. Acid Green 25	V.S.	V.S.
Erio Fast Blue SGR	C.I. Acid Blue 120	S.	V.S.
Polar Yellow 5GN	C.I. Acid Yellow 110	S.S.	V.S.
Polar Yellow 2G	C.I. Acid Yellow 40	S.S.	V.S.
Polar Yellow R	C.I. Acid Orange 63	M.S.	V.S.
Fast Jasmine G	C.I. Acid Yellow 65	S.S.	S.
Polar Orange R	C.I. Acid Orange 45	S.	M.S.
Polar Red G	C.I. Acid Red 85	S.S.	S.
Polar Red GRS	—	M.S.	V.S.
Polar Red RS	C.I. Acid Red 99	M.S.	V.S.
Polar Red RL	C.I. Acid Red 174	M.S.	V.S.
Polar Red B	C.I. Acid Red 167	S.	V.S.
Polar Red BL	C.I. Acid Red 168	V.S.	V.S.
Polar Red R	C.I. Acid Red 99	S.	V.S.
Polar Brilliant Red 5G	C.I. Acid Red 126	V.S.	V.S.
Polar Brilliant Red G	C.I. Acid Red 122	M.S.	V.S.
Polar Brilliant Red 3BN	C.I. Acid Red 131	S.	V.S.
Polar Brilliant Red BN	C.I. Acid Red 130	S.S.	V.S.
Polar Red 3B	C.I. Acid Red 134	V.S.	S.
Polar Brilliant Red 10B	C.I. Acid Violet 54	S.S.	V.S.
Polar Red Brown V	C.I. Acid Red 119	S.S.	V.S.
Neutral Brown RX	C.I. Acid Orange 51	V.S.	S.
Polar Brilliant Violet BL	C.I. Acid Violet 48	V.S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
Polar Brilliant Blue 3R	C.I. Acid Blue 126	S.S.	V.S.
Polar Brilliant Blue RAW	C.I. Acid Blue 80	S.	V.S.
Polar Brilliant Blue GRL	C.I. Acid Blue 143	V.S.	V.S.
Polar Brilliant Blue GAW	Similar to C.I. Acid Blue 127	V.S.	V.S.
Polar Green 2BDE	—	V.S.	V.S.
Polar Grey	C.I. Acid Black 39	S.S.	V.S.
Acid Black HFN	—	M.S.	V.S.
Acid Black HFN (5%)	—	S.S.	V.S.
Acid Black HFN (10%)	—	S.S.	V.S.
Irganol Brilliant Yellow 3GLS	—	M.S.	S.
Irganol Yellow 5GLS	—	S.S.	V.S.
Irganol Red BLS	—	V.S.	V.S.
Irganol Blue BS	—	V.S.	V.S.
Irganol Green B	C.I. Acid Green 40	V.S.	V.S.
	CHROME DYES		
Eriochrome Flavine A	C.I. Mordant Yellow 5	S.S.	V.S.
Eriochrome Yellow G	C.I. Mordant Yellow 16	S.S.	S.
Eriochrome Red 6G	C.I. Mordant Red 12	S.S.	V.S.
Eriochrome Red G	C.I. Mordant Red 17	S.	V.S.
Eriochrome Brilliant Red BL	C.I. Mordant Red 21	S.S.	V.S.
Eriochrome Brown R	C.I. Mordant Brown 33	S.	V.S.
Eriochrome Brown AEB	C.I. Mordant Brown 1	M.S.	V.S.
Eriochrome Blue 2GK	C.I. Mordant Blue 49	V.S.	S.S.
Eriochrome Grey ABE	C.I. Mordant Black 13	R.I.	V.S.
Eriochrome Blue Black B	C.I. Mordant Black 3	V.S.	M.S.
Eriochrome Blue Black B (5%)	C.I. Mordant Black 3	V.S.	M.S.
Eriochrome Blue Black B (10%)	C.I. Mordant Black 3	S.	M.S.
Eriochrome Black T	C.I. Mordant Black 11	V.S.	S.
Eriochrome Black T (8%)	C.I. Mordant Black 11	S.	S.
	METAL-COMPLEX DYES		
Irgalan Yellow GL	C.I. Acid Yellow 114	V.S.	S.S.
Irgalan Yellow 2RL	C.I. Acid Orange 85	V.S.	S.S.
Irgalan Orange RL	C.I. Acid Orange 86	V.S.	S.S.
Irgalan Red 3G	C.I. Acid Red 220	V.S.	R.I.
Irgalan Red 2BL	C.I. Acid Red 219	V.S.	S.S.
Irgalan Brown 2GL	C.I. Acid Brown 44	V.S.	M.S.
Irgalan Brown 2RL	C.I. Acid Brown 45	V.S.	S.S.
Irgalan Brown 7RL	C.I. Acid Brown 47	V.S.	R.I.
Irgalan Dark Brown 5R (4%)	C.I. Acid Brown 48	V.S.	S.
Irgalan Brown 3BL	C.I. Acid Brown 46	V.S.	S.S.
Irgalan Brown FL	—	V.S.	M.S.
Irgalan Rubine RL	C.I. Acid Violet 75	V.S.	M.S.
Irgalan Bordeaux 2BL	C.I. Acid Red 218	V.S.	S.S.
Irgalan Violet 5RL	C.I. Acid Violet 73	V.S.	M.S.
Irgalan Brown Violet DL	C.I. Acid Violet 78	V.S.	M.S.
Irgalan Violet 4BL	C.I. Acid Blue 167	V.S.	S.S.
Irgalan Blue GL	C.I. Acid Blue 166	V.S.	R.I.
Irgalan Blue RL	—	V.S.	S.S.
Irgalan Navy Blue 5RL	—	V.S.	M.S.
Irgalan Navy Blue 2RLS	—	V.S.	M.S.
Irgalan Brilliant Green 3GL	—	V.S.	S.
Irgalan Olive BGL	C.I. Acid Black 64	V.S.	S.S.
Irgalan Grey RL	—	V.S.	S.S.
Irgalan Grey BL	C.I. Acid Black 58	V.S.	S.S.
	General Dyestuff Co.		
	FENAPLEX DYES		
Fenaplex Yellow NR	—	V.S.	M.S.
Fenaplex Orange NR	—	V.S.	S.S.
Fenaplex Red NB	—	V.S.	S.S.
Fenaplex Bordeaux NB	—	V.S.	S.S.
Fenaplex Violet NR	—	V.S.	S.S.
Fenaplex Brown NY	—	V.S.	M.S.
Fenaplex Brown NR	—	V.S.	M.S.
Fenaplex Blue NB	—	V.S.	S.S.
Fenaplex Blue G	—	V.S.	S.S.
Fenaplex Grey 2G	—	V.S.	S.S.

Dye	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
I. B. Holliday & Co. Ltd.			
	ACID DYES		
Fast Neutral Yellow G conc.	C.I. Acid Yellow 65	S.S.–M.S.	S.
Cyanine Fast Yellow 2G	C.I. Acid Yellow 29	S.S.	S.
Cyanine Fast Yellow R	C.I. Acid Yellow 25	S.S.	S.
Cyanine Fast Yellow M	C.I. Acid Yellow 42	S.S.	S.S.
Fast Light Yellow 5GL	C.I. Acid Yellow 17	S.S.	V.S.
Elite Fast Yellow 2G conc.	C.I. Acid Yellow 40	S.S.	V.S.
Elite Fast Orange 4G conc.	C.I. Acid Orange 48	R.I.	V.S.
Elite Fast Orange R	C.I. Acid Orange 45	S.	M.S.–S.
Acetyl Rose 2GL	C.I. Acid Red 1	S.S.	V.S.
Cyanine Fast Red 2G	C.I. Acid Orange 19	S.S.	V.S.
Acetyl Fast Red BG	C.I. Acid Red 37	S.S.	V.S.
Elite Fast Red G	C.I. Acid Red 85	S.S.	M.S.
Elite Fast Red R	C.I. Acid Red 99	M.S.–S.	V.S.
Elite Fast Red B	C.I. Acid Red 167	S.	V.S.
Elite Fast Red 3B	C.I. Acid Red 134	V.S.	S.
Fast Neutral Brown 2R	C.I. Acid Orange 51	S.	V.S.
Alizarine Brilliant Green 5G conc.	C.I. Acid Green 41	V.S.	V.S.
Alizarine Brilliant Green G conc.	C.I. Acid Green 25	V.S.	V.S.
Alizarine Straight Blue ART	C.I. Acid Blue 25	M.S.	V.S.
Alizarine Brilliant Blue B	C.I. Acid Blue 45	S.S.	V.S.
Alizarine Pure Blue B	C.I. Acid Blue 78	M.S.	V.S.
Superlan Blue PFN	—	S.S.	V.S.
Superlan Blue SES	C.I. Acid Blue 37	M.S.	V.S.
Superlan Blue 2G	C.I. Acid Blue 40	S.	V.S.
Superlan Blue R	C.I. Acid Blue 47	M.S.	V.S.
Alizarine Brilliant Violet R	C.I. Acid Violet 43	S.S.	V.S.
Anthraquinone Violet 3R	C.I. Acid Violet 34	R.I.	S.
Cyanine Navy Blue 2RNX	C.I. Acid Blue 113	S.	V.S.
Cyanine Fast Black 4B extra (6%)	C.I. Acid Black 26A	S.	V.S.
Imperial Chemical Industries Ltd.			
	ACID DYES		
Quinoline Yellow A	C.I. Acid Yellow 3	S.S.	S.
Lissamine Fast Yellow 2G	C.I. Acid Yellow 17	R.I.	S.
Metanil Yellow YK	C.I. Acid Yellow 36	R.I.	V.S.
Lissamine Fast Yellow AE	C.I. Acid Orange 3	S.S.	S.
Naphthalene Fast Orange 2G	C.I. Acid Orange 10	R.I.	S.
Naphthalene Orange G	C.I. Acid Orange 7	S.S.	V.S.
Naphthalene Orange RO	C.I. Acid Orange 8	R.I.	M.S.
Croceine Scarlet 3B	C.I. Acid Red 73	S.S.	S.
Naphthalene Scarlet B	C.I. Acid Red 102	R.I.	S.
Naphthalene Scarlet 4R	C.I. Acid Red 18	R.I.	V.S.
Lissamine Fast Scarlet R	—	R.I.	V.S.
Lissamine Fast Red 4G	C.I. Acid Red 30	S.S.	V.S.
Lissamine Fast Red 3G	C.I. Acid Red 5	R.I.	V.S.
Lissamine Fast Red B	C.I. Acid Red 37	S.S.	V.S.
Azo Geranine 2G	C.I. Acid Red 1	S.S.	V.S.
Carmoisine W	C.I. Acid Red 14	S.S.	V.S.
Carmoisine L	C.I. Acid Red 12	R.I.	V.S.
Lissamine Rhodamine G	C.I. Acid Red 50	V.S.	V.S.
Lissamine Rhodamine B	C.I. Acid Red 52	S.–V.S.	V.S.
Solway Rubinol R	C.I. Acid Red 30	S.S.	V.S.
Lissamine Red 6B	C.I. Acid Violet 7	S.S.	V.S.
Lissamine Red 7BP	C.I. Acid Violet 5	S.S.	S.
Solway Violet BR	C.I. Acid Violet 34	M.S.	V.S.
Solway Violet BN	C.I. Acid Violet 34	M.S.	V.S.
Naphthalene Purple A	C.I. Acid Violet 62	R.I.	M.S.
Lissamine Violet 2R	C.I. Acid Violet 1	S.S.	V.S.
Solway Purple R	C.I. Acid Violet 43	S.S.–M.S.	V.S.
Lissamine Fast Violet 2B	C.I. Acid Violet 41	S.S.	V.S.
Solway Blue RN	C.I. Acid Blue 47	S.S.–M.S.	V.S.
Lissamine Ultra Sky R	C.I. Acid Blue 67	S.S.	V.S.
Solway Ultra Blue B	C.I. Acid Blue 25	M.S.	V.S.
Solway Sky Blue B	C.I. Acid Blue 78	S.	V.S.
Solway Blue A	C.I. Acid Blue 69	R.I.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
Solway Blue G	C.I. Acid Blue 37	M.S.	V.S.
Solway Blue 2G	C.I. Acid Blue 40	S.	V.S.
Solway Celestol B	C.I. Acid Blue 27	M.S.	V.S.
Disulphine Blue FFN	C.I. Acid Blue 147	V.S.	V.S.
Solway Green G	C.I. Acid Green 25	V.S.	V.S.
Naphthalene Dark Green A	C.I. Acid Green 20	S.	V.S.
Rufasol Black B (3·5%)	—	R.I.	S.S.
Carbolan Yellow 4G	C.I. Acid Yellow 70	M.S.	S.
Carbolan Yellow 3G	C.I. Acid Yellow 72	R.I.	S.S.
Coomassie Fast Yellow G	C.I. Acid Yellow 85	V.S.	V.S.
Carbolan Yellow R	C.I. Acid Yellow 71	S.	V.S.
Coomassie Yellow R	C.I. Acid Yellow 42	M.S.	M.S.
Coomassie Fast Orange G	C.I. Acid Orange 33	V.S.	V.S.
Carbolan Fawn R	C.I. Acid Brown 49	V.S.	V.S.
Coomassie Brown G	C.I. Acid Brown 22	V.S.	V.S.
Coomassie Fast Brown R	C.I. Acid Orange 51	V.S.	V.S.
Coomassie Fast Scarlet 2G	C.I. Acid Red 140	S.S.	S.
Coomassie Fast Scarlet B	C.I. Acid Red 111	S.	V.S.
Coomassie Red PG	C.I. Acid Red 85	R.I.	M.S.
Coomassie Red R	C.I. Acid Red 99	M.S.	V.S.
Coomassie Red G	C.I. Acid Red 116	R.I.	S.
Carbolan Crimson B	C.I. Acid Red 138	S.S.	S.
Carbolan Crimson 3B	C.I. Acid Red 139	S.	V.S.
Carbolan Violet 2R	C.I. Acid Violet 51	S.S.	V.S.
Coomassie Blue RL	C.I. Acid Blue 92	S.S.	V.S.
Coomassie Blue BL	C.I. Acid Blue 59	S.	V.S.
Coomassie Blue GL	C.I. Acid Blue 102	V.S.	V.S.
Carbolan Brilliant Blue 2R	C.I. Acid Blue 140	V.S.	V.S.
Coomassie Ultra Sky SE	C.I. Acid Blue 112	S.	V.S.
Coomassie Brilliant Blue G	C.I. Acid Blue 90	V.S.	S.
Carbolan Blue R	C.I. Acid Blue 139	S.	V.S.
Carbolan Blue B	C.I. Acid Blue 138	M.S.	V.S.
Coomassie Navy Blue D	C.I. Acid Black 26A	M.S.	V.S.
Coomassie Navy Blue 2RN	C.I. Acid Blue 113	S.	S.
Coomassie Navy Blue GN	C.I. Acid Blue 120	S.	V.S.
Coomassie Navy Blue G	C.I. Acid Blue 118	S.	V.S.
Coomassie Navy Blue G (6%)	C.I. Acid Blue 118	M.S.	V.S.
Coomassie Green T	C.I. Acid Green 19	V.S.	V.S.
Coomassie Green WN	—	V.S.	V.S.
Carbolan Green G	C.I. Acid Green 27	S.	V.S.
Carbolan Brilliant Green 5G	C.I. Acid Green 28	S.	V.S.
Coomassie Fast Grey 3G	C.I. Acid Black 48	V.S.	V.S.
Coomassie Fast Black B (4%)	C.I. Acid Black 24	S.S.	S.
Coomassie Fast Black G (4%)	C.I. Acid Black 21	S.S.	S.
	SOLUBLE DYES FOR CELLULOSE ACETATE		
Solacet Fast Yellow G	—	S.S.	S.S.
Solacet Fast Orange 2GK	C.I. Acid Yellow 64	S.	M.S.
Solacet Fast Scarlet B	C.I. Acid Red 53	S.	M.S.
Solacet Fast Crimson B	C.I. Acid Red 159	S.	M.S.
Solacet Fast Red 5BG	C.I. Acid Red 156	S.	M.S.
Solacet Fast Violet 4R	C.I. Acid Violet 18	S.	R.I.
Solacet Violet R	C.I. Acid Violet 8	V.S.	S.
Solacet Violet B	C.I. Acid Violet 10	V.S.	S.
Solacet Fast Blue 2B	C.I. Acid Blue 14	S.	M.S.
Solacet Navy Blue G	C.I. Acid Blue 30	S.	S.
Solacet Fast Green 2G	C.I. Acid Green 17	V.S.	M.S.
	CHROME DYES		
Solochrome Flavine G	C.I. Mordant Yellow 5	S.S.	V.S.
Solochrome Yellow 3G	C.I. Mordant Yellow 18	S.S.	V.S.
Solochrome Yellow C	C.I. Mordant Yellow 16	S.S.	S.
Solochrome Yellow Y	C.I. Mordant Yellow 20	R.I.	V.S.
Solochrome Yellow 2G	C.I. Mordant Yellow 10	S.S.	V.S.
Solochrome Flavine R	C.I. Mordant Yellow 8	S.	V.S.
Solochrome Yellow 2GN	C.I. Mordant Yellow 12	M.S.	V.S.
Solochrome Orange M	C.I. Mordant Orange 1	S.S.	V.S.
Solochrome Orange GR	C.I. Mordant Orange 6	S.S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations	
		Physical	Chemical
Solochromate Fast Orange 2R	C.I. Mordant Orange 12	V.S.	V.S.
Solochromate Fast Brown 3G	C.I. Mordant Brown 24	S.	S.
Solochrome Brown MO	C.I. Mordant Brown 6	S.	V.S.
Solochrome Brown MG	C.I. Mordant Brown 48	M.S.	V.S.
Solochrome Brown RH	C.I. Mordant Brown 33	M.S.	V.S.
Solochrome Brown M	C.I. Mordant Brown 12	M.S.	V.S.
Solochrome Brown EB	C.I. Mordant Brown 1	S.	V.S.
Solochrome Brown P	C.I. Mordant Brown 31	V.S.	V.S.
Solochrome Brown R	C.I. Mordant Brown 8	V.S.	V.S.
Solochrome Brown RG	C.I. Mordant Brown 29	S.S.	S.
Solochromate Fast Red 3G	C.I. Mordant Red 19	M.S.	V.S.
Solochromate Fast Red G	C.I. Mordant Red 23	V.S.	V.S.
Solochrome Red D	C.I. Mordant Red 14	M.S.	V.S.
Solochrome Red B	C.I. Mordant Red 9	R.I.	V.S.
Solochrome Red ER	C.I. Mordant Red 7	M.S.	V.S.
Alizarine Red A	C.I. Mordant Red 3	M.S.	V.S.
Solochrome Violet R	C.I. Mordant Violet 5	S.	V.S.
Solochromate Fast Violet B	C.I. Mordant Violet 4	M.S.	V.S.
Solochromate Brilliant Violet BR	C.I. Mordant Violet 8	M.S.	V.S.
Solochrome Azurine B	C.I. Mordant Blue 1	S.S.	V.S.
Solochrome Fast Blue B	C.I. Mordant Blue 7	V.S.	S.
Solochrome Green V	C.I. Mordant Green 15	V.S.	V.S.
Solochromate Fast Grey RA	C.I. Mordant Black 15	S.	V.S.
Solochromate Fast Grey B	C.I. Mordant Black 38	M.S.	V.S.
Solway Blue Black B	C.I. Mordant Black 13	M.S.	V.S.
Solochrome Black A	C.I. Mordant Black 1	S.S.	V.S.
Solochrome Black A (5%)	C.I. Mordant Black 1	R.I.	V.S.
Solochrome Black A (10%)	C.I. Mordant Black 1	R.I.	M.S.
Solochrome Black 6BN	C.I. Mordant Black 43	S.	V.S.
Solochrome Black 6BN (5%)	C.I. Mordant Black 43	S.S.	S.
Solochrome Black 6BN (10%)	C.I. Mordant Black 43	R.I.	M.S.
Solochrome Black F	C.I. Mordant Black 5	S.	S.
Solochrome Black F (5%)	C.I. Mordant Black 5	M.S.	S.
Solochrome Black F (10%)	C.I. Mordant Black 5	R.I.	S.S.
Solochrome Black PG	C.I. Mordant Black 7	V.S.	V.S.
Solochrome Black PG (5%)	C.I. Mordant Black 7	S.S.	V.S.
Solochrome Black PG (10%)	C.I. Mordant Black 7	S.S.	V.S.
Solochrome Black PV	C.I. Mordant Black 9	M.S.	V.S.
Solochrome Black PV (5%)	C.I. Mordant Black 9	S.S.	V.S.
Solochrome Black PV (10%)	C.I. Mordant Black 9	S.S.	V.S.
Solochrome Black WDFA	C.I. Mordant Black 11	V.S.	V.S.
Solochrome Black WDFA (5%)	C.I. Mordant Black 11	V.S.	V.S.
Solochrome Black WDFA (10%)	C.I. Mordant Black 11	M.S.	S.
	DIRECT DYES		
Durazol Yellow G	C.I. Direct Yellow 28	V.S.	V.S.
Durazol Flavine R	C.I. Direct Yellow 50	S.	V.S.
Chlorazol Fast Orange R	C.I. Direct Orange 26	S.	V.S.
Chlorazol Fast Red F	C.I. Direct Red 1	R.I.	M.S.
Durazol Red 2B	C.I. Direct Red 81	S.S.	S.
Durazol Blue 2R (1%)	C.I. Direct Blue 71	V.S.	V.S.
	METAL-COMPLEX DYES		
Ultralan Yellow R	C.I. Acid Yellow 99	V.S.	V.S.
Ultralan Orange G	C.I. Acid Orange 74	S.	V.S.
Ultralan Orange R	C.I. Acid Orange 76	S.	V.S.
Ultralan Red R	C.I. Acid Red 180	M.S.	V.S.
Ultralan Red B	C.I. Acid Red 212	S.	V.S.
Ultralan Pink BN	C.I. Acid Red 186	S.	V.S.
Ultralan Bordeaux R	C.I. Acid Red 179	V.S.	V.S.
Ultralan Bordeaux B	C.I. Acid Red 187	V.S.	V.S.
Ultralan Violet 5R	C.I. Acid Violet 58	V.S.	V.S.
Ultralan Blue 2G	—	V.S.	V.S.
Ultralan Navy Blue B	—	V.S.	V.S.
Ultralan Dark Green B	C.I. Acid Green 35	V.S.	V.S.
	AZOIC COMBINATIONS		
4% Brenthol LTR+	*C.I. Azoic Coupling Component 12*		
8% Fast Garnet GBC Base	C.I. Azoic Diazo Component 4	M.S.	R.I.
8% Fast Red KB Base	C.I. Azoic Diazo Component 32	S.S.	R.I.
8% Fast Red RC Base	C.I. Azoic Diazo Component 10	S.S.	R.I.

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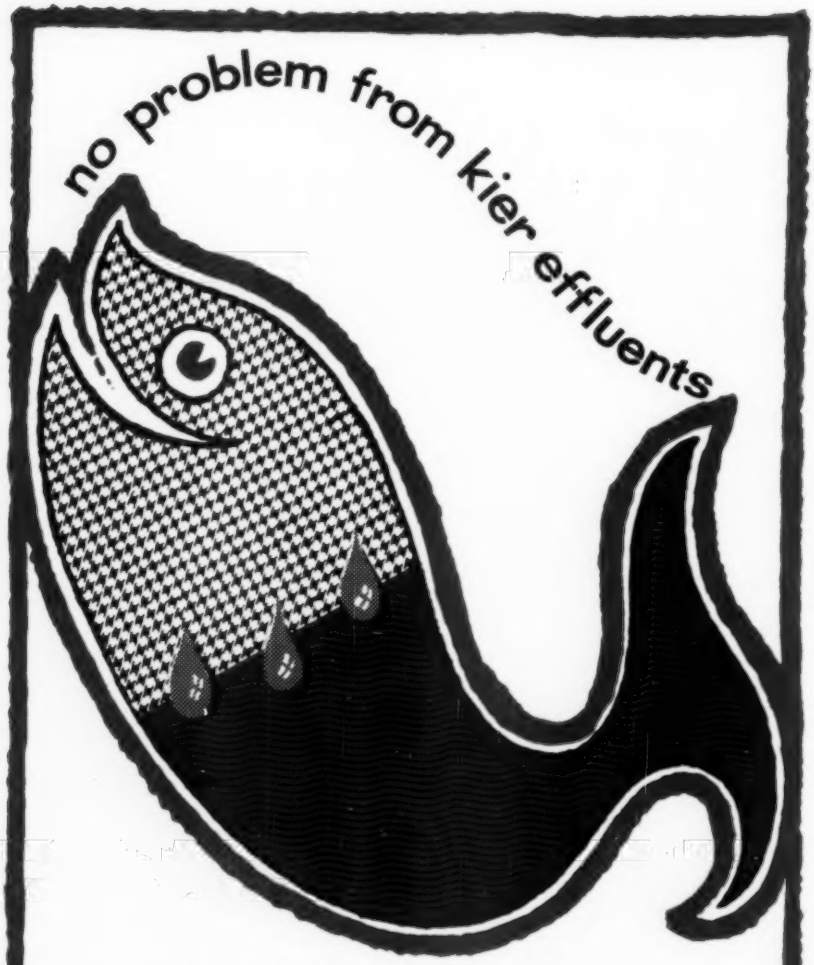

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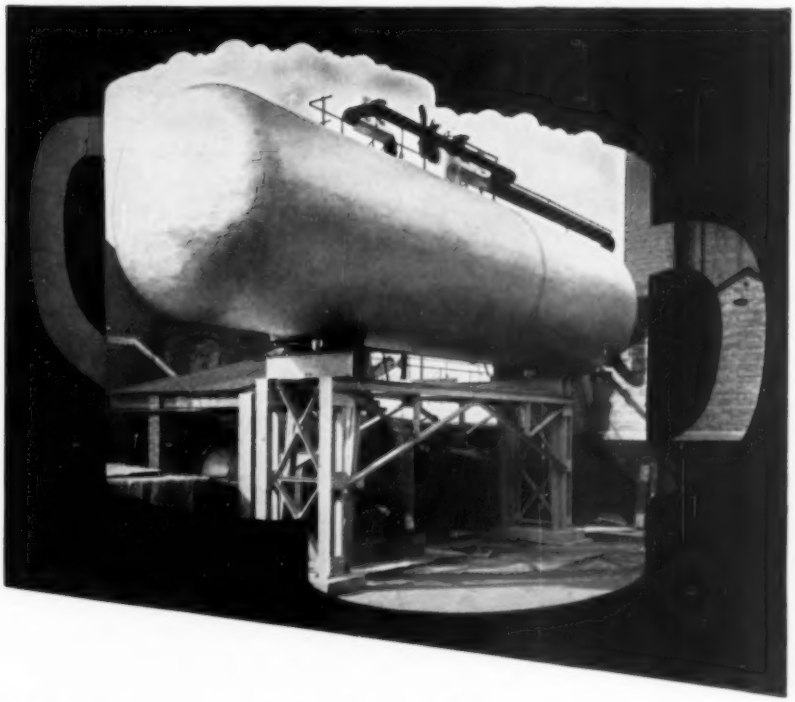

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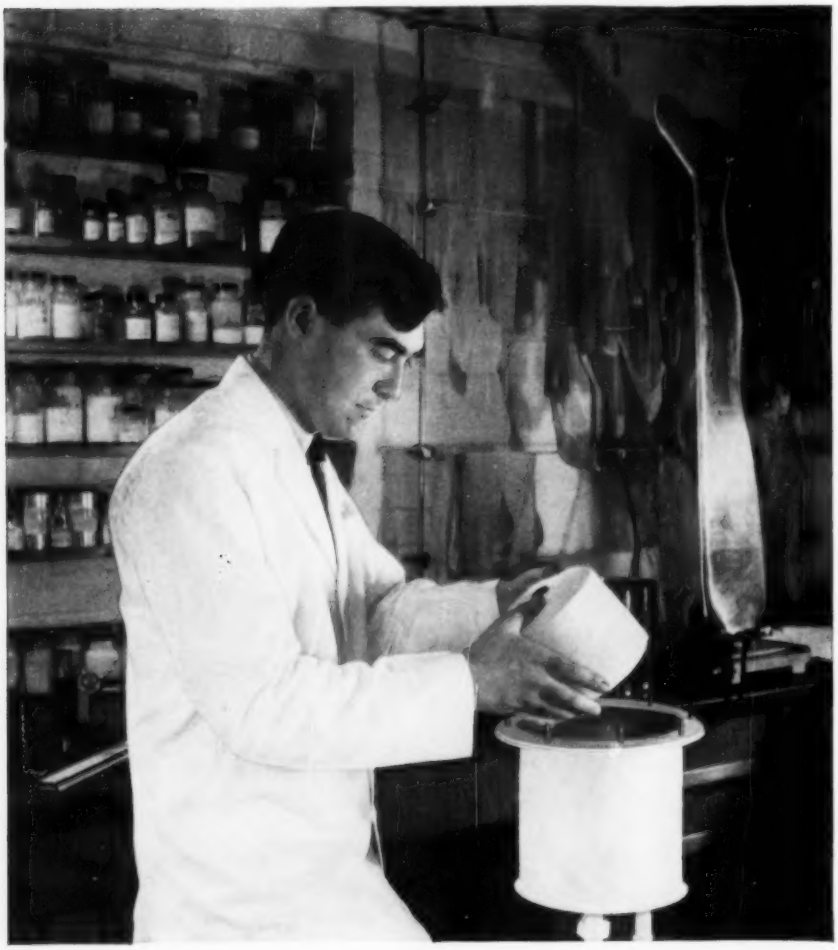

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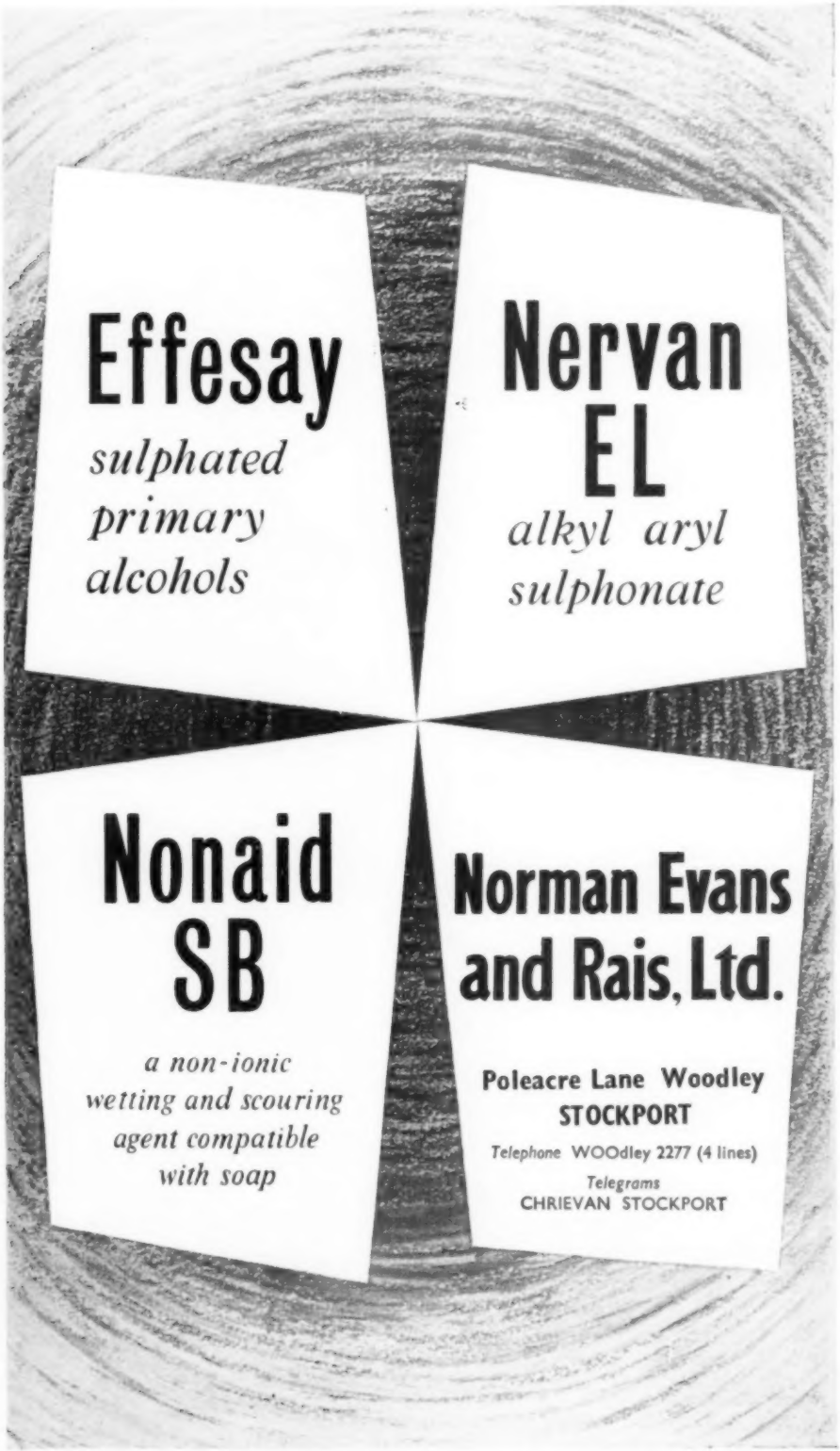
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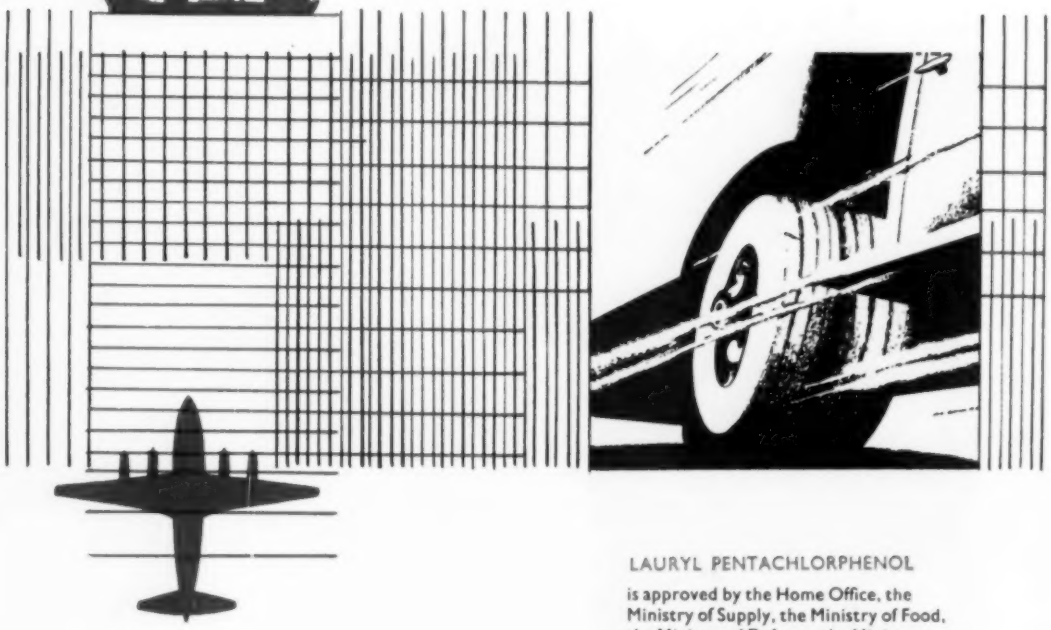

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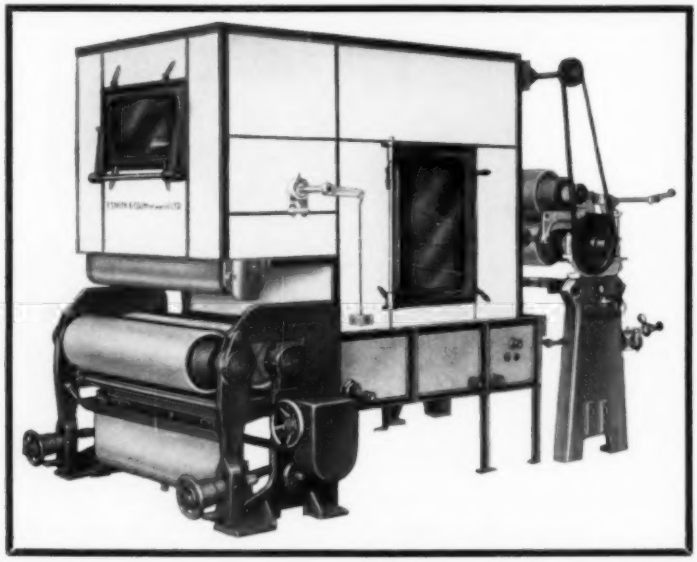

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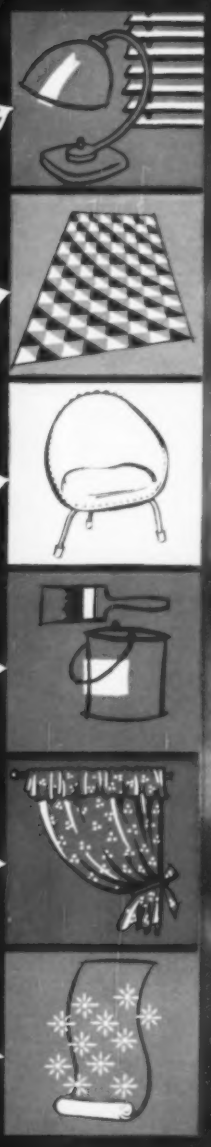

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Just like a boomerang, complaints of poor colour fastness invariably return to the dyer or printer. As claims increase, business is likely to suffer. On the other hand, fast dyed goods not only please the consumer, but also ensure repeat orders. The use of Fast Dyestuffs of BASF is profitable investment.

BASF *Fast Dyes give best results!*

1/469

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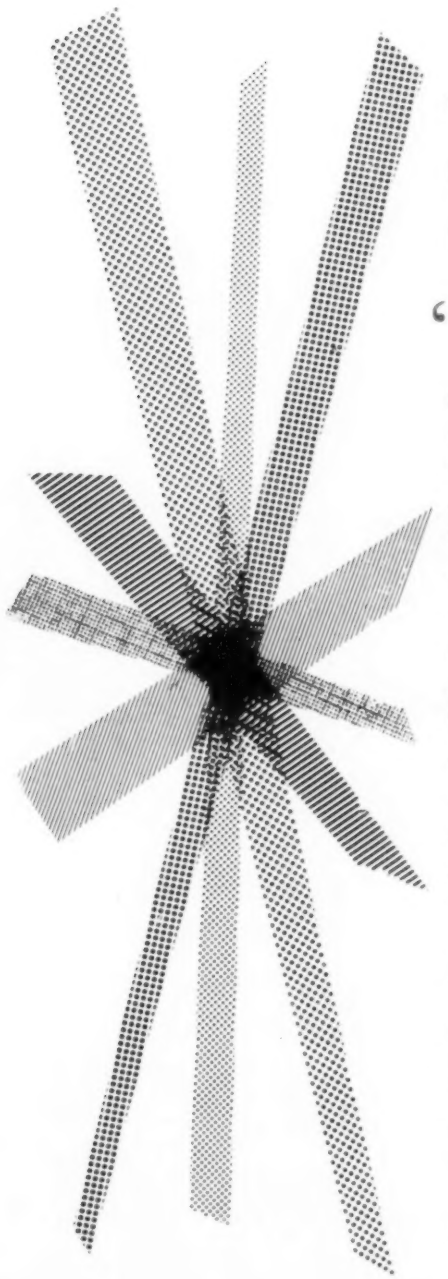

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YET DOES *NOT* DO THIS:

★ Condense in the dyeing machine—Carrier LB is non-volatile

★ Impair the fastness properties of disperse dyes

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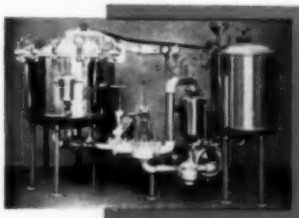
PRESSURE DYEING MACHINES

A complete range of machines for dyeing all types of fibre in every stage of manufacture, including loose, top, beam, hank and package forms. Also rapid package drying machines.



HANK DYEING MACHINES

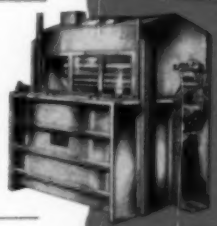
Built in stainless steel in capacities ranging from 25 to 1500 lbs. for all classes of wool, worsted, mixture and linen yarns in hank form. Machines may be coupled together.

LOOSE STOCK DYEING MACHINES

For all classes of loose stock, rags and synthetic fibres. In 3 capacities of 10–50 lbs., 100–250 lbs. and 200–600 lbs. Stainless steel construction.

PIECE GOODS DYEING MACHINES

A comprehensive range of machines available in stainless steel for dyeing all types of woollen or worsted piece goods, silk or rayon fabrics and knitted fabrics in rope form. Also carpet dyeing machines.



ROTARY DYEING MACHINES

Totally enclosed rotating drum machine for dyeing nylon, pure silk, rayon and cotton hose with perfect penetration and uniformity. Stainless steel in 25, 50, 100, and 200 lbs. capacities.

PADDLE DYEING MACHINES

A versatile machine, in stainless steel, for ladies' hose, half hose, and loose articles. Also used for anti-shrink and bleaching. 4 capacities from 12–200 lbs.

DYEING AND FINISHING MACHINES

Builders of dyeing machines for loose stock, hanks, packages, piece-goods, fabric and hose; also finishing machines for all classes of circular knitted and warp loom fabrics and garments. Pre-boarding and finishing machines for nylon hose.

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SP 1

Dye	*Colour Index* No.	Sensitivity to Variations: Physical	Chemical
8% Fast Scarlet RC Base	C.I. Azoic Diazo Component 13	S.S.	R.I.
8% Fast Red TR Base	C.I. Azoic Diazo Component 11	R.I.	R.I.
8% Fast Scarlet GG Base	C.I. Azoic Diazo Component 3	S.S.	R.I.
8% Fast Scarlet G Base	C.I. Azoic Diazo Component 12	M.S.	R.I.
2% Brenthol FO←	*C.I. Azoic Coupling Component 19*		
8% Fast Yellow GC Base	C.I. Azoic Diazo Component 44	R.I.	S.S.
4% Brenthol FO←	*C.I. Azoic Coupling Component 19*		
6% Fast Red TR Base	C.I. Azoic Diazo Component 11	S.S.	R.I.
4% Fast Scarlet GG Base	C.I. Azoic Diazo Component 3	S.	R.I.
6% Fast Red RC Base	C.I. Azoic Diazo Component 10	S.	R.I.
6% Fast Red KB Base	C.I. Azoic Diazo Component 32	S.	R.I.
8% Fast Red GL Base	C.I. Azoic Diazo Component 8	R.I.	S.S.
4% Brenthol BA←	*C.I. Azoic Coupling Component 6*		
8% Fast Yellow GC Base	C.I. Azoic Diazo Component 44	R.I.	R.I.
8% Fast Red KB Base	C.I. Azoic Diazo Component 32	R.I.	R.I.
2% Brenthol DA←	*C.I. Azoic Coupling Component 3*		
4% Fast Scarlet GG Base	C.I. Azoic Diazo Component 3	V.S.	V.S.
4% Fast Red GK Base	C.I. Azoic Diazo Component 8	V.S.	V.S.
3% Brenthol DA←	*C.I. Azoic Coupling Component 3*		
6% Fast Red KB Base	C.I. Azoic Diazo Component 32	V.S.	V.S.
4% Brenthol DA←	*C.I. Azoic Coupling Component 3*		
8% Fast Yellow GC Base	C.I. Azoic Diazo Component 44	V.S.	V.S.
8% Fast Red TR Base	C.I. Azoic Diazo Component 11	S.	S.
8% Fast Red RC Base	C.I. Azoic Diazo Component 10	V.S.	V.S.
2% Brenthol CT←	*C.I. Azoic Coupling Component 8*		
4% Fast Yellow GC Base	C.I. Azoic Diazo Component 44	R.I.	R.I.
4% Brenthol CT←	*C.I. Azoic Coupling Component 8*		
12% Fast Red KB Base	C.I. Azoic Diazo Component 32	S.S.	R.I.
4% Brenthol AN←	*C.I. Azoic Coupling Component 4*		
8% Fast Blue B Base	C.I. Azoic Diazo Component 48	S.S.	R.I.
2% Brenthol MN←	*C.I. Azoic Coupling Component 17*		
4% Fast Yellow GC Base	C.I. Azoic Diazo Component 44	S.S.	R.I.
4% Brenthol MN←	*C.I. Azoic Coupling Component 17*		
8% Fast Red KB Base	C.I. Azoic Diazo Component 32	S.S.	S.S.
3% Brenthol BB←	*C.I. Azoic Coupling Component 10*		
6% Fast Yellow GC Base	C.I. Azoic Diazo Component 44	R.I.	R.I.
4% Brenthol BB←	*C.I. Azoic Coupling Component 10*		
8% Fast Red KB Base	C.I. Azoic Diazo Component 32	S.S.	S.S.
4% Brentacet Scarlet G	—	S.S.	R.I.
4% Brentacet Red	—	S.S.	R.I.
5% Brentacet Bordeaux B	—	S.S.	R.I.
12% Brentacet Black B	—	S.S.	R.I.
	REACTIVE DYES		
Procion Yellow R	—	M.S.	V.S.
Procion Brilliant Red 2B	—	V.S.	V.S.
Procion Blue 3G	—	V.S.	V.S.
	VERILAN DYES		
Verilan Yellow 2GS	—	S.S.	V.S.
Verilan Yellow 2RS	—	M.S.	V.S.
Verilan Orange RS	—	V.S.	V.S.
Verilan Red 5GS	—	V.S.	V.S.
Verilan Violet RBS	—	V.S.	V.S.
Verilan Bordeaux BS	—	V.S.	S.
Verilan Blue BS	—	V.S.	V.S.
Verilan Olive GS	—	V.S.	V.S.
Verilan Brown RS	—	V.S.	V.S.
Verilan Brown GS	—	V.S.	V.S.
Verilan Brown 5GS	—	V.S.	V.S.
Verilan Grey 2BS	—	V.S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
	VAT DYES		
Caledon Gold Orange G (10%)	C.I. Vat Orange 9	S.	M.S.
Caledon Orange 6R (15%)	C.I. Vat Orange 3	S.	M.S.
Caledon Red 2G (10%)	C.I. Vat Red 23	M.S.	M.S.
Caledon Green 2B (10%)	C.I. Vat Green 11	M.S.	M.S.
Caledon Green RC (10%)	C.I. Vat Green 6	V.S.	V.S.
Caledon Jade Green 2G (10%)	C.I. Vat Green 2	S.	S.S.
Caledon Jade Green XN (10%)	C.I. Vat Green 1	S.	S.
Caledon Dark Blue G (15%)	C.I. Vat Blue 16	S.	M.S.
E. I. du Pont de Nemours & Co. Inc.			
	METAL-COMPLEX DYES		
Capracyl Yellow 3RD	C.I. Acid Orange 64	V.S.	S.
Capracyl Yellow NW	—	V.S.	S.
Capracyl Orange R	C.I. Acid Orange 60	V.S.	S.
Capracyl Red B	C.I. Acid Red 182	V.S.	S.
Capracyl Red BB	C.I. Acid Red 178	V.S.	S.
Capracyl Blue G	C.I. Acid Blue 165	V.S.	S.
Capracyl Brown RD	C.I. Acid Brown 29	S.	M.S.
Capracyl Black N	—	S.	M.S.
Sandoz Ltd.			
	ACID DYES		
Xylene Light Yellow 2G	C.I. Acid Yellow 17	S.S.	V.S.
Xylene Fast Yellow 2GP	C.I. Acid Yellow 29	M.S.	V.S.
Xylene Fast Yellow WS	C.I. Acid Yellow 97	S.S.	V.S.
Xylene Fast Orange PO	C.I. Acid Orange 28	S.S.	V.S.
Xylene Fast Orange RT	—	V.S.	V.S.
Croceine Brilliant Scarlet 3BC	C.I. Acid Red 73	R.I.	V.S.
Sulphanine Scarlet GWL	C.I. Acid Red 111	M.S.	V.S.
Xylene Milling Red 3BLN	—	V.S.	V.S.
Xylene Milling Red B	C.I. Acid Red 166	V.S.	V.S.
Azo Rhodine 2G	C.I. Acid Red 1	S.S.	V.S.
Azo Rubinole 3GP	C.I. Acid Red 57	S.	V.S.
Brilliant Alizarine Milling Red FBL	C.I. Acid Red 143	V.S.	V.S.
Brilliant Alizarine Light Violet FFR	C.I. Acid Violet 31	V.S.	V.S.
Brilliant Alizarine Milling Violet FBL	C.I. Acid Violet 48	V.S.	V.S.
Xylene Fast Violet P3R	C.I. Acid Violet 47	S.	V.S.
Brilliant Alizarine Milling Blue 2RL	C.I. Acid Blue 126	S.S.	V.S.
Brilliant Alizarine Light Blue 3F	C.I. Acid Blue 54	S.S.	V.S.
Alizarine Light Blue 4GL	C.I. Acid Blue 23	S.	V.S.
Xylene Fast Blue BL	C.I. Acid Blue 59	M.S.	S.–V.S.
Xylene Fast Blue FF	Similar to C.I. Acid Blue 61	V.S.	V.S.
Xylene Milling Blue 6G	C.I. Acid Blue 148	V.S.	V.S.
Xylene Blue VS	C.I. Acid Blue 1	V.S.	V.S.
Xylene Fast Yellow P	C.I. Acid Yellow 61	M.S.	V.S.
Xylene Fast Orange P	C.I. Acid Orange 43	S.S.	V.S.
Xylene Fast Red P	C.I. Acid Red 118	S.S.	S.
Xylene Fast Bordeaux P	—	M.S.	V.S.
Xylene Fast Blue PR	C.I. Acid Blue 129	M.S.	V.S.
Xylene Fast Blue P	C.I. Acid Blue 82	M.S.	V.S.
Xylene Fast Grey P	C.I. Acid Black 50	M.S.	V.S.
	CHROME DYES		
Metomega Chrome Yellow ME	C.I. Mordant Yellow 30	M.S.	V.S.
Metomega Chrome Orange ML	C.I. Mordant Orange 8	M.S.	V.S.
Metomega Chrome Red GM	C.I. Mordant Red 36	V.S.	S.S.
Metomega Chrome Bordeaux 2BL	C.I. Mordant Red 38	S.	V.S.
Metomega Chrome Cyanine BLL	C.I. Mordant Blue 7	V.S.	S.
Metomega Chrome Green BLL	C.I. Mordant Green 29	V.S.	V.S.
Metomega Chrome Brown RLL	C.I. Mordant Brown 63	V.S.	S.
Metomega Chrome Brown 3GL	C.I. Mordant Brown 50	V.S.	S.
Chromosol Yellow GD	C.I. Mordant Yellow 34	S.S.	V.S.
Omega Chrome Red B	C.I. Mordant Red 7	M.S.	V.S.
Omega Chrome Brown 2R conc.	C.I. Mordant Brown 33	S.	V.S.
Omega Chrome Brown EB	C.I. Mordant Brown 1	S.	V.S.
Alizarine Blue OCRB Extra	C.I. Mordant Blue 5	M.S.	V.S.
Omega Chrome Grey BLC	C.I. Mordant Black 44	S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations: Physical	Chemical
Omega Chrome Black T	C.I. Mordant Black 11	S.	V.S.
Omega Chrome Black T (5%)	C.I. Mordant Black 11	S.S.	V.S.
Omega Chrome Black T (10%)	C.I. Mordant Black 11	R.I.	M.S.
	METAL-COMPLEX DYES		
Lanasyn Yellow GLN	C.I. Acid Yellow 112	V.S.	R.I.
Lanasyn Yellow 3GL	C.I. Acid Yellow 111	V.S.	R.I.
Lanasyn Red BL	C.I. Acid Red 215	V.S.	S.S.
Lanasyn Red 2GL	C.I. Acid Red 216	V.S.	S.S.
Lanasyn Bordeaux RL	C.I. Acid Red 217	V.S.	S.S.
Lanasyn Dark Violet RL	C.I. Acid Violet 66	V.S.	R.I.
Lanasyn Brown 3RL	C.I. Acid Brown 30	V.S.	S.S.
Lanasyn Brown RL	C.I. Acid Brown 28	V.S.	S.
Lanasyn Grey BL	C.I. Acid Black 58	V.S.	S.S.
The Yorkshire Dyeware & Chemical Co. Ltd.			
	ACID DYES		
Milling Yellow H5G	C.I. Acid Yellow 44	M.S.	V.S.
Milling Yellow 3G	C.I. Acid Yellow 56	M.S.	V.S.
Fast Light Yellow 2G	C.I. Acid Yellow 17	S.S.	S.
Fast Light Yellow E	C.I. Acid Orange 3	M.S.	V.S.
Acid Yellow T	C.I. Acid Yellow 23	R.I.	V.S.
Fast Light Orange G	C.I. Acid Orange 10	S.S.	V.S.
Orange II	C.I. Acid Orange 7	R.I.	V.S.
Sulphonol Orange R	C.I. Acid Orange 45	M.S.	V.S.
Croceine Scarlet M	C.I. Acid Red 73	S.S.	V.S.
Scarlet 2RE	C.I. Acid Red 102	S.S.	V.S.
Fast Red A	C.I. Acid Red 88	S.S.	V.S.
Acid Levelling Red 2G	C.I. Acid Red 1	S.S.	V.S.
Fast Light Red GL	—	S.	V.S.
Fast Light Red BG	C.I. Acid Red 37	S.S.	V.S.
Acid Levelling Red 6B	C.I. Acid Violet 7	S.S.–M.S.	V.S.
Carmoisine	C.I. Acid Red 14	R.I.–S.S.	V.S.
Supra Red 3B	C.I. Acid Red 35	M.S.	V.S.
Sulphonol Light Scarlet GL	—	V.S.	V.S.
Fast Azo Violet RL	C.I. Acid Violet 1	S.S.	V.S.
Acid Violet 6BN	—	V.S.	S.
Acid Violet 4BNS	C.I. Acid Violet 17	V.S.	V.S.
Acid Violet 5BNS	C.I. Acid Violet 24	V.S.	S.
Fast Acid Violet R	C.I. Acid Violet 9	V.S.	V.S.
Sulphonol Brown 5R	C.I. Acid Orange 51	V.S.	V.S.
Resorcine Brown	C.I. Acid Orange 24	S.	V.S.
Alizarine Brilliant Blue B	C.I. Acid Blue 45	M.S.	V.S.
Alizarine Brilliant Blue RL	C.I. Acid Blue 47	M.S.	V.S.
Alizarine Supra Blue B	C.I. Acid Blue 25	M.S.	V.S.
Indigo Carmine	C.I. Acid Blue 74	S.	V.S.
Acid Green MV	C.I. Acid Green 16	V.S.	V.S.
Brilliant Acid Green B	C.I. Acid Green 9	S.–V.S.	V.S.
Patent Blue V	C.I. Acid Blue 1	V.S.	V.S.
Patent Blue A	C.I. Acid Blue 5	V.S.	V.S.
Sulphonol Navy 5RX	C.I. Acid Blue 113	S.	V.S.
Sulphonol Black BR	C.I. Acid Black 24	V.S.	V.S.
Sulphonol Black BR (5%)	C.I. Acid Black 24	S.S.–M.S.	V.S.
Sulphonol Black BR (10%)	C.I. Acid Black 24	S.S.	M.S.
Naphthol Blue Black	C.I. Acid Black 1	S.	V.S.
Naphthol Blue Black (5%)	C.I. Acid Black 1	M.S.	V.S.
Naphthol Blue Black (10%)	C.I. Acid Black 1	S.S.–M.S.	V.S.
	CHROME DYES		
Durochrome Yellow C	C.I. Mordant Yellow 16	S.S.	S.–V.S.
Durochrome Yellow 2G	C.I. Mordant Yellow 10	S.S.	V.S.
Durochrome Yellow 2RN	C.I. Mordant Orange 1	S.S.–M.S.	V.S.
Durochrome Orange R	C.I. Mordant Orange 10	M.S.	V.S.
Durochrome Red B	C.I. Mordant Red 7	M.S.	V.S.
Durochrome Violet B	C.I. Mordant Violet 5	S.	V.S.
Durochrome Brown EB	C.I. Mordant Brown 1	S.	S.
Durochrome Brown RH	C.I. Mordant Brown 33	M.S.	V.S.
Durochrome Azurol B	C.I. Mordant Blue 1	S.S.	V.S.
Durochrome Blue OCRA	C.I. Mordant Blue 5	V.S.	V.S.

Dye	*Colour Index* No.	Sensitivity to Variations Physical	Chemical
Durochrome Green B	C.I. Mordant Green 15	V.S.	V.S.
Alizarine Cyanine Green G	C.I. Acid Green 25	S.	V.S.
Durochrome Black T	C.I. Mordant Black 11	V.S.	M.S.
Durochrome Black T (5%)	C.I. Mordant Black 11	V.S.	S.
Durochrome Black T (10%)	C.I. Mordant Black 11	M.S.	V.S.
Durochrome Black A	C.I. Mordant Black 1	S.S.	V.S.
Durochrome Black A (5%)	C.I. Mordant Black 1	R.I.	V.S.
Durochrome Black A (10%)	C.I. Mordant Black 1	R.I.	M.S.
Durochrome Black PV	C.I. Mordant Black 9	V.S.	V.S.
Durochrome Black PV (5%)	C.I. Mordant Black 9	S.	V.S.
Durochrome Black PV (10%)	C.I. Mordant Black 9	M.S.	V.S.
Alizarine Blue Black B	C.I. Mordant Black 13	S.	V.S.
Alizarine Blue Black B (5%)	C.I. Mordant Black 13	M.S.	V.S.
Alizarine Blue Black B (10%)	C.I. Mordant Black 13	S.S.	V.S.

DISPERSE DYES

Ciba Ltd. and The Clayton Dyestuffs Co. Ltd.

Dye	*Colour Index* No.	Sensitivity to Variations* at 60°c. Ph.	60°c. Ch.	85°c. Ph.	85°c. Ch.	100°c. Ph.	100°c. Ch.
Cibacet Yellow GN	C.I. Disperse Yellow 8	M.S.	R.I.	S.S.	R.I.	—	—
Cibacet Yellow 2GC	C.I. Disperse Yellow 3	M.S.	R.I.	S.S.	R.I.	—	—
Cibacet Yellow GBA extra	C.I. Disperse Yellow 3	S.	R.I.	S.S.	R.I.	—	—
Cibacet Yellow GGR	—	M.S.	R.I.	S.S.	R.I.	—	—
Cibacet Orange 2R	C.I. Disperse Orange 3	V.S.	R.I.	R.I.	R.I.	—	—
Cibacet Orange 4R	C.I. Disperse Orange 8	V.S.	R.I.	S.S.	R.I.	—	—
Cibacet Brilliant Scarlet RG	C.I. Disperse Red 12	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Cibacet Scarlet 2B	C.I. Disperse Red 1	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Cibacet Red 2G	C.I. Disperse Red 17	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Cibacet Red BBS	C.I. Disperse Red 24	V.S.	R.I.	V.S.	R.I.	S.	R.I
Cibacet Red E3B	C.I. Disperse Red 15	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Cibacet Rubine R	C.I. Disperse Red 13	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Cibacet Violet E2R	C.I. Disperse Violet 1	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Cibacet Violet 5R	C.I. Disperse Violet 10	V.S.	R.I.	S.	R.I.	S.	R.I.
Cibacet Violet RB	C.I. Disperse Violet 15	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Cibacet Brilliant Blue BG New	C.I. Disperse Blue 3	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Cibacet Blue F3R	C.I. Disperse Blue 3	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Cibacet Sapphire Blue G	C.I. Disperse Blue 1	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Cibacet Sapphire Blue 4G	C.I. Disperse Blue 16	S.	R.I.	M.S.	R.I.	S.S.	R.I.
Cibacet Blue Green EB	—	V.S.	R.I.	V.S.	R.I.	S.	R.I.
Cibacet Navy Blue CBN	C.I. Disperse Blue 29	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Cibacet Green CG	C.I. Disperse Green Mixture	V.S.	R.I.	S.	R.I.	S.	R.I.
Cibacet Green C2G	C.I. Disperse Green Mixture	V.S.	R.I.	M.S.	R.I.	S.	R.I.
Cibacet Brown BNH	—	V.S.	R.I.	S.	R.I.	S.	R.I.
Cibacet Brown NH	—	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Cibacet Grey NH	—	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Nylocet Brown TN	C.I. Disperse Brown Mixture	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Nylocet Brown MN	C.I. Disperse Brown Mixture	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Nylocet Grey BN	C.I. Disperse Grey Mixture	V.S.	R.I.	S.	R.I.	M.S.	R.I.

The Geigy Co. Ltd.

Setacyl Yellow G	C.I. Disperse Yellow 3	S.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Setacyl Yellow BS	—	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Setacyl Yellow 5G Supra	C.I. Disperse Yellow 19	M.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Setacyl Orange RE	C.I. Disperse Orange 3	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Setacyl Orange 4R	C.I. Disperse Orange 8	V.S.	R.I.	S.S.	R.I.	R.I.	R.I.
Setacyl Scarlet R	—	V.S.	R.I.	S.	R.I.	S.	R.I.
Setacyl Scarlet 2B	—	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Setacyl Red 2B	C.I. Disperse Red 13	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Setacyl Red BN	—	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Setacyl Pink 3B	C.I. Disperse Red 24	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.
Setacyl Violet R	C.I. Disperse Violet 1	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Setacyl Violet B	Similar to C.I. Disperse Violet 4	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Setacyl Violet 4RT Supra	C.I. Disperse Violet 12	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Setacyl Blue 2GS	C.I. Disperse Blue 1	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Setacyl Brilliant Blue BG	C.I. Disperse Blue 3	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Setacyl Blue 4GS Supra	C.I. Disperse Blue 16	S.	R.I.	M.S.	R.I.	S.S.	R.I.

* Ph. = Physical
Ch. = Chemical

Dye	*Colour Index* No.	Sensitivity to Variations at 60°c. Ph.	60°c. Ch.	85°c. Ph.	85°c. Ch.	100°c. Ph.	100°c. Ch.
Setacyl Blue 6GN	—	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.
Setacyl Discharge Blue GNN Supra	C.I. Disperse Blue 30	V.S.	R.I.	V.S.	R.I.	V.S.	R.I.
Setacyl Navy Blue CGN	C.I. Disperse Blue 29	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Setacyl Black GM	C.I. Disperse Black 13	V.S.	R.I.	S.	R.I.	M.S.	R.I.
L. B. Holliday & Co. Ltd.							
Supracet Yellow 2G	C.I. Disperse Yellow 16	S.S.	R.I.	R.I.	R.I.	—	—
Supracet Fast Yellow G	C.I. Disperse Yellow 3	S.S.	R.I.	R.I.	R.I.	—	—
Supracet Golden Orange GR	C.I. Disperse Orange 13	S.	S.S.	V.S.	S.S.	S.	M.S.
Supracet Orange R	C.I. Disperse Orange 11	S.	R.I.	S.S.	R.I.	—	—
Supracet Fast Orange G	C.I. Disperse Orange 3	V.S.	R.I.	S.S.	R.I.	—	—
Supracet Fast Scarlet B	C.I. Disperse Red 1	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Supracet Fast Scarlet G	C.I. Disperse Red 19	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Supracet Fast Scarlet 2G	C.I. Disperse Orange 1	V.S.	R.I.	M.S.	R.I.	R.I.	R.I.
Supracet Brilliant Red 2B	C.I. Disperse Red 15	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Supracet Fast Red G	C.I. Disperse Red 17	V.S.	R.I.	S.	R.I.	—	—
Supracet Pink R	C.I. Disperse Red 9	S.	R.I.	S.S.	R.I.	—	—
Supracet Fast Pink 2R	C.I. Disperse Red 4	S.	R.I.	S.S.	R.I.	—	—
Supracet Fast Pink 3B	C.I. Disperse Red 11	V.S.	R.I.	S.S.	R.I.	—	—
Supracet Fast Crimson B	C.I. Disperse Red 13	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Supracet Violet 2B	C.I. Disperse Violet 4	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Supracet Brilliant Violet 3R	C.I. Disperse Violet 1	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Supracet Violet R	C.I. Disperse Violet 12	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Supracet Fast Blue 2G	C.I. Disperse Blue 14	S.–V.S.	R.I.	S.S.	R.I.	—	—
Supracet Deep Blue R	C.I. Disperse Blue 1	V.S.	R.I.	S.S.	R.I.	—	—
Supracet Brilliant Blue BG	C.I. Disperse Blue 3	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Supracet Brilliant Blue 2GN	C.I. Disperse Blue 1	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Supracet Navy Blue R	C.I. Disperse Navy Mixture	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Supracet Green 3G	C.I. Disperse Green Mixture	V.S.	R.I.	S.S.	R.I.	—	—
Supracet Brown B	C.I. Disperse Brown Mixture	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Supracet Fast Brown 3R	C.I. Disperse Orange 5	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Supracet Fast Brown BT	C.I. Disperse Brown Mixture	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Imperial Chemical Industries Ltd.							
Dispersol Yellow 3G	C.I. Disperse Yellow 4	M.S.	R.I.	R.I.	R.I.	—	—
Dispersol Fast Yellow G	C.I. Disperse Yellow 3	M.S.	R.I.	R.I.	R.I.	—	—
Dispersol Fast Yellow GR	C.I. Disperse Yellow 39	V.S.	R.I.	S.S.	R.I.	—	—
Dispersol Fast Yellow A	C.I. Disperse Yellow 1	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Brilliant Yellow 6G	C.I. Disperse Yellow 13	S.S.	R.I.	R.I.	R.I.	—	—
Dispersol Fast Orange B	C.I. Disperse Orange 13	S.	R.I.	S.	R.I.	—	—
Dispersol Fast Orange Brown R	C.I. Disperse Orange 5	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Dispersol Fast Orange A	C.I. Disperse Orange 1	S.	R.I.	S.S.	R.I.	—	—
Dispersol Fast Orange G	C.I. Disperse Orange 3	S.	R.I.	R.I.	R.I.	—	—
Duranol Orange G	C.I. Disperse Orange 11	V.S.	R.I.	S.S.	R.I.	—	—
Dispersol Fast Scarlet B	C.I. Disperse Red 1	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Duranol Red G	—	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Red GN	C.I. Disperse Red 9	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Red 2B	C.I. Disperse Red 15	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Red X3B	C.I. Disperse Red 11	V.S.	R.I.	S.S.	R.I.	—	—
Dispersol Fast Red R	C.I. Disperse Red 19	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Dispersol Fast Crimson B	C.I. Disperse Red 13	V.S.	R.I.	V.S.	R.I.	S.S.	R.I.
Duranol Brilliant Violet BR	C.I. Disperse Violet 8	V.S.	R.I.	M.S.	R.I.	—	—
Duranol Brilliant Violet B	C.I. Disperse Violet 4	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Violet 2R	C.I. Disperse Violet 1	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Duranol Blue 2G	C.I. Disperse Blue 24	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Duranol Brilliant Blue G	C.I. Disperse Blue 14	S.	R.I.	S.S.	R.I.	—	—
Duranol Brilliant Blue B	C.I. Disperse Blue 3	V.S.	R.I.	R.I.	R.I.	—	—
Duranol Brilliant Blue CB	C.I. Disperse Blue 1	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Blue GN	—	V.S.	R.I.	S.S.	R.I.	—	—
Duranol Blue Green B	C.I. Disperse Blue 7	V.S.	R.I.	V.S.	R.I.	S.	R.I.
Multamine Navy Blue G	—	V.S.	R.I.	M.S.	R.I.	—	—
Multamine Navy Blue 2B	—	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Multamine Green 2G	—	V.S.	R.I.	S.S.	R.I.	—	—
Multamine Brilliant Green B	—	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.
Multamine Dark Green B	—	V.S.	R.I.	S.S.	R.I.	—	—
Multamine Brown 4R	—	V.S.	R.I.	S.S.	R.I.	—	—
Multamine Brown G	—	V.S.	R.I.	S.S.	R.I.	—	—

Dye	*Colour Index* No.	Sensitivity to Variations at 60°c. Ph.	60°c. Ch.	85°c. Ph.	85°c. Ch.	100°c. Ph.	100°c. Ch.
Multamine Brown R	—	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Multamine Hosiery Brown OR	—	V.S.	R.I.	S.S.	R.I.	—	—
Multamine Hosiery Brown BV	—	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Multamine Brown 2G	—	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Multamine Grey B	—	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Multamine Grey G	—	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Multamine Black B	—	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Sandoz Ltd.							
Artisil Yellow GN	C.I. Disperse Yellow 8	M.S.	R.I.	S.S.	R.I.	R.I.	R.I.
Artisil Yellow 2GN	C.I. Disperse Yellow 3	S.S.	R.I.	R.I.	R.I.	R.I.	R.I.
Artisil Yellow RGFL	C.I. Disperse Yellow 36	V.S.	R.I.	M.S.	M.S.	S.S.	S.
Artisil Orange 2RP	C.I. Disperse Orange 3	S.	R.I.	R.I.	R.I.	R.I.	R.I.
Artisil Orange NR	—	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Orange GFL	C.I. Disperse Orange 20	V.S.	R.I.	S.	R.I.	S.	M.S.
Artisil Orange RFL	C.I. Disperse Orange 21	V.S.	R.I.	V.S.	R.I.	S.	M.S.
Artisil Scarlet GP	C.I. Disperse Red 2	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Scarlet GFL	C.I. Disperse Red 43	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.
Artisil Scarlet GFP	—	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Red BP	C.I. Disperse Red 24	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Artisil Rubine GP	—	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Artisil Violet 2RP	C.I. Disperse Violet 1	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Violet 3BP	—	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Blue BSQ	C.I. Disperse Blue 3	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Artisil Blue BG	—	S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Blue 4GP	C.I. Disperse Blue 16	S.	R.I.	S.	R.I.	M.S.	R.I.
Artisil Blue BRPW	—	V.S.	R.I.	S.S.	R.I.	M.S.	R.I.
Artisil Blue SAP	C.I. Disperse Blue 1	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Artisil Navy Blue BNR	—	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Navy Blue BIW	—	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Artisil Navy Blue BNP	C.I. Disperse Blue 29	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Blue Green GP	C.I. Disperse Blue 7	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.
Artisil Green DG	—	S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Brown NR	—	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Brown NS	—	V.S.	R.I.	S.S.	R.I.	S.S.	R.I.
Artisil Nylon Brown B	—	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Artisil Grey NG	—	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
The Yorkshire Dyeware & Chemical Co. Ltd.							
Serisol Fast Yellow N5RD	C.I. Disperse Yellow 7	M.S.	R.I.	R.I.	R.I.	—	—
Serisol Fast Yellow 8GGL	—	M.S.	R.I.	M.S.	R.I.	—	—
Serisol Fast Yellow 5GD	C.I. Disperse Yellow 5	M.S.	R.I.	R.I.	R.I.	—	—
Serisol Fast Yellow GD	C.I. Disperse Yellow 3	S.S.	R.I.	R.I.	R.I.	—	—
Serisol Fast Yellow GWD	—	S.	R.I.	S.	R.I.	—	—
Serisol Fast Yellow GGL	—	M.S.	R.I.	S.S.	R.I.	—	—
Serisol Yellow N	—	S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Orange GD	C.I. Disperse Orange 3	V.S.	R.I.	R.I.	R.I.	—	—
Serisol Fast Orange RD	C.I. Disperse Orange 1	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Orange YL	C.I. Disperse Orange 11	S.	R.I.	R.I.	R.I.	—	—
Serisol Fast Scarlet GD	C.I. Disperse Red 19	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Serisol Fast Scarlet BD	C.I. Disperse Red 1	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Serinyl Brilliant Scarlet RD	C.I. Disperse Red 6	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Serisol Fast Red 2RDX	C.I. Disperse Red 17	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Red BRD	—	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Red 2B	C.I. Disperse Red 15	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Red 3BL	C.I. Disperse Violet 6	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Brilliant Red X3B	C.I. Disperse Red 11	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Red BGL	—	V.S.	R.I.	V.S.	R.I.	M.S.	R.I.
Serisol Fast Pink B	C.I. Disperse Red 3	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Crimson BD	C.I. Disperse Red 13	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Serisol Brilliant Violet 2R	C.I. Disperse Violet 1	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Serisol Fast Violet 6B	C.I. Disperse Violet 4	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Brilliant Blue G	C.I. Disperse Blue 14	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Serisol Brilliant Blue ABG	C.I. Disperse Blue 37	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Brilliant Blue BG	C.I. Disperse Blue 3	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Brilliant Blue 2B	C.I. Disperse Blue 23	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Serisol Brilliant Blue R	C.I. Disperse Blue 22	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.

Dye	*Colour Index* No.	Sensitivity to Variations at 60°C. Ph.	60°C. Ch.	85°C. Ph.	85°C. Ch.	100°C. Ph.	100°C. Ch.
Serisol Fast Blue BRL	C.I. Disperse Blue 19	V.S.	R.I.	M.S.	R.I.	R.I.	R.I.
Serinyl Blue 2G	C.I. Disperse Blue 1	V.S.	R.I.	M.S.	R.I.	M.S.	R.I.
Serilene Dark Blue G	C.I. Disperse Blue 35	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Blue Green BW	C.I. Disperse Blue 7	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Serisol Fast Green NB	C.I. Disperse Green Mixture	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Serisol Fast Green N2G	C.I. Disperse Green Mixture	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Brilliant Green 3G	C.I. Disperse Green Mixture	S.	R.I.	S.	R.I.	S.S.	R.I.
Serisol Brilliant Green B	C.I. Disperse Green Mixture	S.	R.I.	M.S.	R.I.	—	—
Serinyl Brilliant Green 2G	C.I. Disperse Green Mixture	V.S.	R.I.	S.S.	R.I.	—	—
Serinyl Fast Green BL	C.I. Disperse Green Mixture	V.S.	R.I.	S.	R.I.	—	—
Serisol Dark Brown HWL	C.I. Disperse Brown Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Red Brown HWL	C.I. Disperse Brown Mixture	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Brown BTN	C.I. Disperse Brown Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Fast Brown RL	C.I. Disperse Brown Mixture	V.S.	R.I.	S.S.	R.I.	—	—
Serinyl Brown R	C.I. Disperse Brown Mixture	V.S.	R.I.	S.	R.I.	M.S.	R.I.
Serinyl Hosiery Brown GN	C.I. Disperse Brown Mixture	V.S.	R.I.	S.	R.I.	S.S.	R.I.
Serinyl Hosiery Brown RN	C.I. Disperse Brown Mixture	V.S.	R.I.	S.S.	R.I.	—	—
Serisol Fast Navy Blue BBN	C.I. Disperse Navy Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Fast Navy Blue GN	C.I. Disperse Navy Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Fast Navy Blue AR	C.I. Disperse Navy Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serinyl Fast Navy Blue B	C.I. Disperse Navy Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Fast Grey J	C.I. Disperse Grey Mixture	V.S.	R.I.	M.S.	R.I.	S.S.	R.I.
Serisol Fast Grey LS	C.I. Disperse Grey Mixture	V.S.	R.I.	R.I.	R.I.	—	—
Serinyl Hosiery Grey GN	C.I. Disperse Grey Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serinyl Fast Grey HWL	C.I. Disperse Grey Mixture	V.S.	R.I.	M.S.	R.I.	—	—
Serisol Fast Grey NS	C.I. Disperse Grey Mixture	V.S.	R.I.	S.S.	R.I.	—	—

We wish to express our thanks to the directors of British Nylon Spinners Ltd. for permission to publish this paper, and our appreciation of the very valuable help and co-operation of all persons within B.N.S. and in the trade with whom this work has been discussed.

BRITISH NYLON SPINNERS LTD.
PONTYPOOL
MONMOUTHSHIRE

(*MS. received 17th June 1957*)

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Discussion

Mr. W. L. LANGTON: Would the lecturers like to assume the prophetic mantle of Elijah and tell us whether they have a small boy who could stand on the battlements of Pontypool and look through the clear, hot sky and see a small cloud of hope (even smaller than a man's hand would do) that such monumental works as this would be unnecessary?

Mr. PETERS: Although close control is exercised by the yarn producer, by the very nature of things it is impossible to guarantee that the yarn is absolutely free from any variation. Even if, in the foreseeable future, such a perfect yarn were produced, variations in subsequent processes could introduce factors which would affect the dyeing of the fibre. We therefore consider that dye classifications such as we have made will always be of some value.

Mr. H. W. PARTRIDGE: Will the authors' assessments of the sensitivity of dyes to physical differences in nylon produced by variation in draw ratio hold good for physical variations produced by other means, such as differences in conditions of steaming or dry-heat setting?

Mr. PETERS: The introduction of physical structure differences between yarns by using different draw ratios for each was adopted solely as a matter of convenience. All the evidence we have collected shows that, no matter how physical structure variations are introduced, their effect is always to alter dyeing rate. An increase in degree of orientation, whether produced by a higher draw ratio or by tensions during processing which are not removed prior to dyeing, will always result in a reduced rate of dyeing. The assessments of the sensitivities of dyes to physical variations will then hold good no matter how the variations are introduced.

Dr. W. L. LEAD: Can yarn containing these predetermined irregularities be made available to others wishing to make further trials along these lines?

Mr. PETERS: In general, the special fabric is not freely available. However, in certain specific cases it might be possible to supply limited quantities. We should prefer to discuss any such arrangement on an individual basis.

Mr. P. MURPHY: What degree of chemical and physical variation can be expected from bulk production yarns?

Mr. G. K. MECKLENBURGH: It is important to record the fact that a difference in amine end-group content of 1 microequivalent per gram is insufficient to cause a discernible dye difference between two yarns in a nylon fabric, even in the colour to which the eye is most sensitive. Mr. Murphy may be reassured that control of amine end-groups within any one merge of nylon yarn is such that any stripiness due to chemical variations should not arise. The responsibility of the yarn producer in this matter is fully accepted. Control of physical variations is the responsibility of all those who handle nylon yarn, including the various sections of the trade, as well as the yarn producer. We have been studying this problem for a long time, and significant improvements are constantly being adopted in yarn manufacture. Control of textile operations in the trade is equally important, since quite large physical irregularities can be caused by incorrect yarn processing.

Mr. MURPHY: Is the degree of "normal" variation great enough to alter the classification of a dye graded e.g. as "relatively insensitive".

Mr. TURNER: The deliberately introduced variations in the experimental fabric are greater than would be expected in a commercial fabric. The degree of "normal" variation would, therefore, not be sufficient to alter the classification of a particular dye. We must, however, emphasise the important part played by dyeing conditions. If the variation between yarns in a commercial fabric is small, then unsatisfactory dyeing conditions will show up stripiness. If dyeing conditions cannot easily be improved (e.g. by enclosing jigs), dye selection becomes even more important.

COMMUNICATIONS

The Determination and the Significance of Crystallite Size in Regenerated Cellulose Fibres

D. N. TYLER and N. S. WOODING

Determinations of accessibility and total crystalline content have been made for a number of regenerated cellulose fibres. Moisture sorption has been used as a measure of cellulose accessibility, and total crystalline content has been estimated from density measurements.

It is suggested that the results may be interpreted as showing differences in the average cross-sectional area of crystalline regions.

An attempt is made to correlate these differences with the properties of the fibres produced by various methods of manufacture.

1. INTRODUCTION

The wide variety of properties possessed by the regenerated cellulose fibres, depending upon their method of production, is well known. The properties of several such fibres are listed in Table I. It is believed that these properties reflect structural differences which are related to the methods of production of the different fibres.

It is generally accepted that in cellulose the chains of anhydroglucose units are in many different relative arrangements ranging from disordered, or amorphous, to highly ordered, or crystalline. Accepting this picture of cellulose structure, there will be a gradual transition between crystalline regions, commonly referred to as *crystallites*, and amorphous regions. Such a system might be described in terms of a spectrum of continuously changing degrees of structural order. It is therefore only a first approximation to regard such regions as mutually exclusive, although this view is a useful simplification which has been adopted in the present paper for convenience of calculation. Furthermore, determination of the relative amounts of crystalline and amorphous cellulose in a fibre will give a result which is dependent upon the method used. Thus most of the methods which have been proposed for such determinations, such as acid hydrolysis, oxidation, thallation, and deuterium exchange, give a measure of the accessibility of the cellulose to reaction under the particular conditions prevailing. In addition to such chemical methods, there are two physical methods, based upon X-ray diffraction and upon the determination of fibre density, which are considered to reflect the crystalline : amorphous ratio less ambiguously. It must be emphasised, in reference to crystallites and amorphous regions, that these terms are defined both by the assumptions made and by the experimental methods used.

A survey shows that, although estimates of the total crystallinity of regenerated cellulose fibres have been made by a number of workers, there have been few attempts to estimate crystallite size. Kast [1] has taken data from Mark *et al.*[2] and Howsmon [3] and has derived average crystallite sizes for a number of cellulose fibres. Mann and Marrinan [4] have compared percentage of amorphous cellulose, as defined and determined by their infrared technique, in the residue from the acid hydrolyses of Fortisan and cotton with estimates of crystallite size made by workers from electron-microscopic examinations of similar materials. Morehead and Sisson [5] have suggested, from general considerations, that crystallite size is likely to vary in different viscose rayons. Hermans and Heikens [6] reach a similar conclusion from the results of some acid hydrolysis measurements.

The present paper describes some experiments designed to investigate differences in crystalline content and average crystallite size in a number of regenerated cellulose fibres. Crystallinities have been determined from fibre densities, and the accessibilities of the same fibres have been determined by means of moisture sorption measurements, the results of which were converted to

TABLE I

The Properties of some Regenerated Cellulose Fibres

Fibre	Tenacity (g./denier)		Extension (%)		Relaxation† on Wetting (%)
	Conditioned*	Wet	Conditioned*	Wet	
Fortisan X36 (BrC)	7·1	6·1	7·2	9·0	0
Fibre G (DuP)	5·4	3·8	6·0	7·3	0
Durafil A (Courtaulds)	5·6	4·0	7·2	7·4	0
Durafil B (Courtaulds)	5·2	3·7	12·0	15·6	0
Tenasco (Courtaulds)	3·4	2·1	10·1	21·0	9·4
Tenasco 35 (Courtaulds)	4·0	2·5	10·5	21·0	11·8
Tenasco Super 70 (Courtaulds) ...	4·1	3·1	13·5	25·0	9·5
Tenasco Super 105 (Courtaulds) ...	5·3	4·2	12·5	24·0	12·0
Normal textile viscose rayon ...	2·2	1·1	19·9	27·5	<0·5
Ammonium-sulphate-spun rayon...	2·4	1·0	7·0	6·2	0

* Conditioned yarn tests were carried out with the yarn in equilibrium with an atmosphere at 65% R.H. and 70°F.

† The relaxation given in the last column refers to the percentage change in length which occurs when the yarns are wetted and allowed to dry in a freely relaxed state.

accessibilities by means of a value for the accessibility of a standard sample determined by deuterium exchange. These results have been interpreted by regarding the accessibility as being composed of two parts: one, due to the non-crystalline cellulose, can be obtained from the crystallinity; the other, which can then be found from the results by difference, is due to the surface hydroxyls of crystalline regions and is related to both crystallinity, which is known, and crystallite size.

2. EXPERIMENTAL

(i) *Materials*

The fibres used were freed from soluble non-cellulosic material by prolonged washing of small skeins in warm (60°C.) and cold distilled water. The skeins were dried to a low moisture content in an air oven at 70–80°C.

(ii) *Estimation of Accessibility*

Accessibilities were determined from equilibrium moisture sorption regain data. It has been inferred by Mark *et al.*[2] and confirmed by Mann and Marrinan[7] that the accessibility of hydroxyl groups in cellulose may be determined by the exchange of deuterium for hydrogen between the hydroxyl groups and liquid deuterium oxide. This reaction is predominantly reversible. They also state that the differences in the degree of exchange found between vapour-phase and liquid-phase deuteration at equilibrium are differences of rate only, although by taking advantage of the differences in rate an estimate can be made of both total and amorphous accessibility. Hence it seems highly probable that the sorption regain of moisture, as measured at equilibrium, at any given relative humidity, is linearly dependent upon the accessibility to liquid deuterium oxide, also measured at equilibrium.

Howsmon[3] has compared his results with those of Mark[2] and has shown that a linear relation exists between the deuterium oxide accessibility as determined by Mark and the equilibrium sorption regain as determined by Howsmon for a series of different, but similar, fibre samples.

Mark[2] gives values of 41% and 46% for the accessibility of a sample of cotton. The sample of cotton used in the present work had a regain of 7·1% at 60% R.H. and 25°C. Equilibrium moisture sorption values have been converted to accessibilities by taking a mean value of 43·5% for the accessibility of the cotton sample used here.

The equilibrium moisture-sorption isotherms were determined for a number of fibres, including the sample of cotton already described. It was found that the sorption ratio, defined as the equilibrium regain for a given fibre divided by the equilibrium regain for cotton at the same relative humidity, was constant over the range 20–80% R.H. at 25°C. (Table II). Outside this range the accuracy of the experimental method was insufficient to yield reliable values.

In view of the constancy of the sorption ratio, it is permissible to calculate the accessibility from the determination of equilibrium moisture sorption at one fixed relative humidity. Methods involving a final drying in an air oven are either inaccurate or extremely laborious. We have therefore chosen to determine a portion of the sorption isotherm for each sample. In this way the sorption regains obtained are based directly on the weight of bone-dry cellulose.

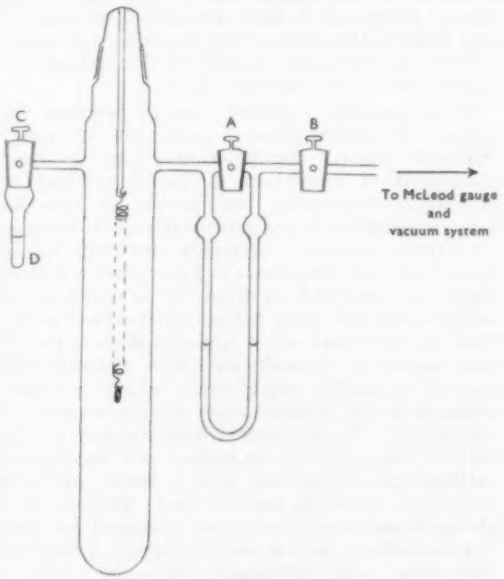

FIG. 1— Moisture Sorption Apparatus

The apparatus used for the determination of moisture sorption isotherms is shown diagrammatically in Fig. 1. After inserting the fibre sample, mounted on the calibrated spring, into the apparatus, taps *A*, *B*, and *C* were opened, and the distilled water in *D* was outgassed in the usual way. Tap *C* was then closed, and the apparatus pumped down to a pressure of less than 0·001 mm. of mercury until the bottom of the spring (marked

TABLE II

Sorption Ratio, relative to Texas Cotton, over a Range of Relative Humidity at 25°C.

Fibre	Relative Humidity (%)					
	30	40	50	60	70	80
Tenasco 35 (Courtaulds)	1·88	1·90	1·89	1·90	1·88	1·85
Tenasco 35, washed and redried three times	1·88	1·84	1·88	1·89	1·92	—
Durafil (Courtaulds)	1·65	1·65	1·64	1·66	1·65	1·62
Ammonium-sulphate-spun yarn ...	—	1·68	1·71	1·70	1·68	1·70
Fortisan H (BrC)	1·26	1·27	1·28	1·30	1·31	1·30

with wax to facilitate reading) reached an upper equilibrium position. This position represented the dry weight of the sample. The dry weight obtained in this way was identical with the dry weight of some of the samples determined by drying to equilibrium in a stream of hot dry nitrogen and weighing in sealed glass bulbs. After noting this position, tap *A* was closed, and a suitable small amount of water vapour admitted through tap *C*. The position of the spring was observed until it reached a new (lower) equilibrium position. After noting this and the water vapour pressure as given by the differential manometer, the procedure was repeated to give a second point on the isotherm. During an experiment the whole apparatus to the left of tap *B* (Fig. 1) was immersed in a water thermostat maintained at $25 \pm 0{\cdot}1$°c. The vacuum system was provided by a two-stage rotary oil pump and traps cooled to −78°c.

The springs used were of silica (sensitivity 25 cm./g.) and later of Pyrex glass (sensitivity 60–70 cm./g.). In both cases the maximum load which could be supported was about 1 g. At no time did the load exceed 0·25 g. The silica springs were calibrated in air and the glass springs *in vacuo*, using platinum riders. It was feared that the glass springs might creep under load, but after loading and unloading several times before use, no indication of creep was detected. All readings were taken with a cathetometer.

The manometric fluid was a sample of Apiezon oil B*, and the saturated vapour pressure of water at 25°c. was 372·5 mm. of this oil. The value was derived from the measured specific gravity and checked directly against mercury in the apparatus using a double differential manometric system.

All fibre samples used in this investigation had been dried down to low regain during production. To ensure that a reproducible value was being determined, one fibre sample was washed and redried (as described in § 2(*i*)) four times. The isotherm for this sample was identical with that for a similar sample washed and dried once only.

(*iii*) *Estimation of Crystallinity*

Since the appreciable scatter of X-rays by the amorphous regions of cellulose precludes the use of this method for the accurate estimation of crystallinity when it is less than about 50%, the density of the fibre has been taken as a measure of crystalline content. For the purpose of calculation it is assumed that the fibre may be regarded as being made up of cellulose which is either crystalline or amorphous, each phase having a unique density.

The density of 100% crystalline material may be calculated from a knowledge of the unit cell. This has been done for cellulose II and for native cellulose I, using the data of Hermans [8] and Mark [9], the values being 1·592 (cellulose I) and 1·583 (cellulose II). Furthermore, the X-ray method is sufficiently accurate to give a reliable measure of the crystalline content of cotton. The cotton sample used here had a density of 1·551 g./c.c. at 25°c., and from X-ray measurements has been taken to have a crystallinity of 70% [10]. Thus two reliable points are known for the density–crystallinity graph of cellulose I. Extrapolation to zero crystallinity has enabled a value (1·455 g./c.c.) to be obtained for the density of completely amorphous cellulose. Using this point, a straight line relating density and percentage of crystalline cellulose II has been drawn (Fig. 2). This method of determining the density of amorphous cellulose seems preferable to the assumption made elsewhere [11] that the ratio of the densities of crystalline and amorphous cellulose is the same as that observed for *tert.*-butyl alcohol (where both quantities may be determined experimentally). Although the procedure used here is arbitrary and the absolute crystallinities estimated may be in error, it is considered that the relative values of crystallinity are correct.

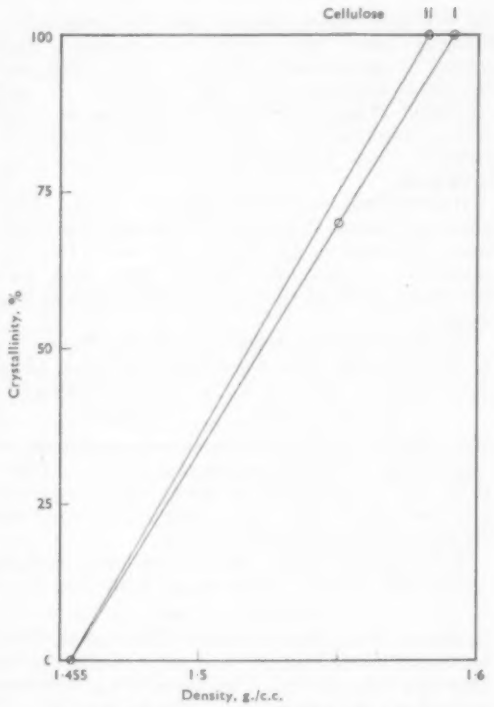

FIG. 2.—Relation between Density and Crystallinity

Two methods have been used for the measurement of fibre density. When the yarn was homogeneous (i.e. contained no visible vacuoles when immersed in methyl salicylate and viewed under the microscope) direct measurement was used. For these samples determination by the density-column method at 25°c. was preferred, since evidence exists which suggests that some penetration of the specimen occurs when thermal flotation methods are employed. The columns, which were composed of benzene–carbon tetrachloride mixtures, were calibrated by the introduction of glass floats of known density. Results were reproducible to $\pm 0{\cdot}001$ g./c.c. (i.e. about ± 1% crystallinity). Before introduction into the column, the dried samples were prepared

* W. Edwards & Co. (London) Ltd.

by refluxing under toluene and then repeatedly washing under hot carbon tetrachloride. This served to ensure easy wetting of the sample and complete elimination of any trapped air and moisture. It also meant that the samples, wet with carbon tetrachloride, rose to their equilibrium position, thus minimising the risk of air contamination.

It is unfortunate that the densities of some of the fibres may not be determined in this direct manner, since they contain microscopically visible inhomogeneities of structure (vacuoles filled with air). For fibres such as these an indirect method was used.

The two principal refractive indices of the fibre in the bone-dry state were calculated from those determined at 65% R.H., using the relation [12]—

$$n_0 = 1 + 1{\cdot}170\,(n_{65} - 1) - 0{\cdot}0715$$

The validity of this expression was confirmed by determining refractive indices at 2, 30, 55, and 65% R.H. for a representative fibre, whose moisture sorption curve had been determined over this range of relative humidity.

The bone-dry refractive indices were used to give a value for n_{iso}, where n_{iso} is defined by [12]—

$$n_{iso} = \tfrac{1}{3}(n_{\parallel} + 2n_{\perp})$$

$n_{\parallel}$ and $n_{\perp}$ being the refractive indices of the fibre for light polarised parallel and perpendicular to the fibre axis respectively. This value of n_{iso} was then used in the expression of Gladstone and Dale—

$$\frac{n_{iso} - 1}{d} = \text{constant}$$

The constant was determined by carrying out density d and optical measurements on similar fibres which were apparently free from air holes (Table III). The justification for this procedure is largely empirical and, until the influence of molecular orientation on fibre density has been fully investigated, must be accepted with reserve.

It will be appreciated that the possible presence of submicroscopic pores in samples, the densities of which were determined directly, must affect the reliability of results. The problem is rendered still more complex by the lack of definition of the boundary between loosely packed amorphous regions and submicroscopic pores.

(*iv*) *Other Measurements*

TENACITY AND EXTENSIBILITY—These properties were determined by well known methods using suitable serimeters.

REFRACTIVE INDEX—Refractive indices were determined by the Becke line technique, using as immersion liquids suitable mixtures of tricresyl phosphate and dibutyl phthalate, or solutions of diphenylamine (stabilised with 1% hydroquinone as anti-oxidant) in tricresyl phosphate. It was necessary to use this technique for many of the fibres used here, because of the presence of many vacuoles within the fibre. However, although some doubt has been cast upon the suitability of this technique as a method for the determination of the refractive index of the whole fibre substance, investigations in this laboratory have shown that the results obtained by the Becke line and fibre refractometer methods are very similar for fibres having no skin–core difference (J. D. Griffiths, private communication). The fibres containing vacuoles, for which the Becke line method was used, showed no skin–core difference.

WATER OF IMBIBITION—This is expressed as a weight percentage on the oven-dry weight of cellulose, and is the amount of water retained by the sample, previously soaked in distilled water at 25°C., after centrifuging at 1000***g*** for 5 min.

LEVELLING-OFF DEGREE OF POLYMERISATION—The acid hydrolysis procedure used in this laboratory (B. M. King, private communication) was similar to that described by Battista *et al.*[13], with the modification that soluble products of hydrolysis were continuously removed. The vessel in which hydrolysis was carried out contained a sintered-glass plate to retain the sample, a small

TABLE III

Accessibility and Crystallinity of some Regenerated Cellulose Fibres

Fibre	Moisture Regain 60% R.H., 25°C. (%)	Accessibility (%)	Density (g./c.c.)	Crystalline Cellulose II (%)	Accessibility Factor of Crystalline Region	Size of Crystallite (A.G.U. in side of square cross-section)	Birefringence (65% R.H., 25°C.)
Fortisan H (BrC)	9·05	55·5	—	49‡	0·09	42	0·045
Fibre G (DuP)	10·45	64·0	1·526*	55·5 (53‡)	0·32	7·5	0·046
Durafil A (Courtaulds)	11·5	70·6	1·513	46·0	0·36	6·5	0·044
Durafil B (Courtaulds)	12·0	73·5	1·513	46·0	0·42	5·3	0·044
Tenasco (Courtaulds)	12·9	79·1	1·509	42·9	0·51	3·9	0·032
Tenasco 35 (Courtaulds)	13·4	82·3	1·509*	42·9	0·58	3·1	0·032
Tenasco Super 70 (Courtaulds) ...	14·4	88·3	1·496†	32·5	0·64	2·5 (2·0§)	0·033
Tenasco Super 105 (Courtaulds) ...	14·1	86·4	1·508†	41·5	0·67	2·0 (2·0§)	0·037
Super Cordura 258 (DuP) ...	13·3	81·5	1·502†	37·3	0·50	3·8 (3·6§)	0·035
Super Rayflex (American Viscose Corpn.)	13·9	85·1	1·495†	31·5	0·53	3·6 (2·5§)	0·036
Ammonium-sulphate-spun yarn	11·95	73·2	1·518	49·0	0·45	4·8	0·034
Normal textile viscose rayon ...	12·5	76·6	1·512	45·2	0·48	4·3	0·027

* The density of this sample was measured directly; the density calculated from birefringence (see text) was identical with this measured value.
† Calculated from birefringence data.
‡ X-Ray determination.
§ Values bracketed in this way calculated assuming 40% crystalline cellulose II.

flow of the acid hydrolysing solution being maintained through this vessel.

The degrees of polymerisation of the acid hydrolysis residues were determined from the viscosities of solutions in cupriethylenediamine. Intrinsic viscosities were converted to degrees of polymerisation using the constants given by Mark *et al.*[14].

3. RESULTS AND DISCUSSION

(i) *Accessibility*

The accessibilities listed in Table III, calculated as described from the equilibrium moisture regain data, and being based on the accessibility of cotton determined in a liquid deuterium oxide–water mixture, are clearly related to this state. This method was preferred to methods based on chemical reactivity, as the values of accessibility determined by the latter are influenced to an unknown extent by swelling and by recrystallisation phenomena. In methods dependent upon regain of moisture and exchange with deuterium oxide the fibre is examined under conditions very similar to those frequently occurring in fibre utilisation.

TABLE IV

Accessibilities (%) determined by Different Workers

Fibre	Mark [2]	Howsmon [3]	Authors' Results
Fibre G	67	72	64
Textile rayon ...	68	79	77
High-tenacity rayon	86	87	79

The values obtained may be compared with those given by Mark [2] and by Howsmon [3] for the appropriate fibres. Fibre G, textile rayon, and high-tenacity rayon are the only fibres known to be similar in the two cases. Despite the fact that the results in Table IV represent three different samples of each type of fibre, there is some measure of agreement.

The accessibility values given by Mark [2] are not true equilibrium values, since they represent the extent of exchange between deuterium oxide and hydroxyl groups of cellulose after 4 hr. under given conditions. Furthermore, the residual water content of the samples was arbitrarily assumed to be 0·5%. It has been found that in fact the residual water content of cellulose dried as described by Mark varies from 0·1 to 0·6%, depending upon the type of fibre. Since the results of Howsmon [3] are based numerically on those of Mark, these criticisms apply to both sets of results. The accessibilities given in Table III are based upon the 4-hr. accessibility for the sample of cotton used by Mark. Both the results of Mark and other work in this laboratory (B. M. King and I. Walsh, personal communication) have shown that, although the 4-hr. value is not identical with the equilibrium value for viscose rayons, it is more nearly identical with the equilibrium value for samples of cotton.

None of the materials used by Mann and Marrinan [7] is comparable with those used in these investigations. The material described by these authors as "viscose" was in the form of films, which were first coagulated in ammonium sulphate and then regenerated in dilute acid.

The results given in Table III show that this group of regenerated cellulose fibres possesses accessibilities which range from 55 to 89%. The implications of these results are discussed in § 4, but it may be noted that the values of accessibility found for different fibres seem to be linked with their method of preparation.

(ii) *Crystallinity*

Some comment has already been made on the methods used for crystallinity determination. It is unfortunate that the values calculated from the optical properties of the fibre are considered to be the least reliable, for it is this series of fibres which shows the highest accessibility. These fibres have the highest work of rupture of any which have so far been regenerated from viscose solutions.

The values found show that there is appreciable variability in the total crystallinity of these different viscose rayon fibres. Hermans [10, 15] has suggested that the total crystallinity of all regenerated cellulose fibres, except Fortisan and Fibre G, is approximately the same, and estimates a value of 40% for this quantity. However, the results presented here do not support this postulate, and suggest that the total crystallinity is dependent upon the regeneration conditions used, although the range of crystallinity is somewhat restricted, being 35–50% crystalline content for the fibres studied.

(iii) *Interpretation of the Results*

Following Mark [2], the relationship between percentage accessibility A and the percentage crystallinity a may be written—

$$A = (100 - a) + \sigma a$$

The first term, $(100 - a)$, gives the contribution of the amorphous cellulose to the accessibility, whilst the second term represents the contribution of non-amorphous material; σ, the proportion of the crystallites which are accessible, is clearly related to crystallite size.

Average crystallite sizes have been calculated from the accessibility and crystallinity results and are listed in Table III as the number of A.G.U. (anhydroglucose units) in the side of a crystallite of square cross-section. Where values for the crystalline fraction were determined from the optical constants, or where no value was measured, the calculation of average crystallite size has been carried out using a value of 40% for a. Such values are enclosed in brackets in Table III. The values given in Table III are based on the following assumptions—

(*A*) The ratio of length to breadth of the crystallites is high, so that end effects are small and may be neglected. Values for mean crystallite length in cellulose fibres are available from two sources. Measurements of levelling-off degree of polymerisation for cellulose subjected to acid hydrolysis should give an upper limit for average crystallite length. Some published values are given in Table V, together with values obtained in

TABLE V

Levelling-off Degrees of Polymerisation (in A.G.U.)

Viscose Rayon Tyre Yarns	Viscose Rayon Textile Yarns	Durafil and Ammonium-sulphate-spun Yarns	Fortisan	Fibre G	Reference
15–30	30–50	—	40–60	40–60	[13]
45	—	—	—	—	[16]
75–100	75–100	—	—	—	[17]
110	110	—	—	—	[18]
20±2	—	30±2	30±2	—	(*)

* King, B. M., *Personal communication.*

this laboratory (B. M. King, personal communication). Although the values found by different workers vary considerably, partly owing to the use of different constants in the Mark–Houwink equation relating degree of polymerisation and intrinsic viscosity, it will be seen that the assumption made here is, to a first approximation, justifiable.

TABLE VI

Microfibrillar Lengths (A.) from Electron Microscopy

Viscose Rayon Tyre Yarns	Viscose Rayon Textile Yarns	Fortisan and Fibre G	Reference
240	240	334	[19]
110–120	110–120	—	[20]

Ribi [20] and Morehead [19] have estimated the length of the ultimate particles visible in electron micrographs of peptised hydrocellulose residues. These authors suggest that the dimensions of these particles are related to the crystallite dimensions in the original fibre. Some values are listed in Table VI. Again, these measurements show that the estimated crystallite length is many times greater than the width.

(*B*) The crystallites are of square cross-section. Kratky [21] has shown that the crystallites in regenerated cellulose are lamellar in form, and Hermans [22] has adduced evidence to support this suggestion. At present, however, it is not possible to state with certainty what the cross-sectional shape of the crystallite is. This being so, the present assumption seems to be satisfactory as a basis of comparison, since the use of other models has but small effect on the conclusions reached here.

(*C*) In all the fibres studied the accessibility of anhydroglucose units in the surface of a crystallite is equivalent to $\frac{2}{3}$ of the total hydroxyl groups in the surface. Again, it is not known what the form of the hydrogen bonding is in the surface of crystalline regions. The results of the present calculations are changed in magnitude, but not in relative order, by assigning a different degree of hydroxyl group accessibility to the surface of the crystallites. It is to be noted that the second part of this assumption, namely, that the degree of crystallite accessibility is the same in all the fibres considered here, is the more important.

(*D*) The crystalline lattice of cellulose II is not penetrated by water. It has been reported that X-ray studies show that the lattice of crystalline cellulose II is penetrated by water [23–25]. In some cases this has been interpreted as showing that well defined hydrates are formed [26]. Other workers conclude that the extent of lattice widening is variable. From the results referred to it seems likely that, although some specimens show that the lattice of cellulose II expands on wetting, this expansion is variable, and is not to be interpreted as due to the formation of definite hydrates throughout the crystalline cellulose II. The observations seem to be more in keeping with the penetration of imperfect or fringe crystalline areas by water. Calculations made here ignore the penetration of the lattice by water.

It is apparent from the results that the average crystallite size varies widely amongst the regenerated cellulose fibres. As has been indicated, assumptions *B*, *C*, and *D* above are not necessarily correct, and hence the average values given in Table III serve to indicate only how average crystallite size varies; the absolute values might be different, were the above assumptions changed or the value of a changed. It is considered, however, that the results demonstrate the possible importance of a structural factor which has hitherto received limited attention.

The question of absolute crystallite size has been referred to above. The importance of crystallite shape and perfection is not clearly apparent. Certainly, variations of accessibility and crystallinity of the type found could be due to changes in either or both these factors.

Mention has already been made of crystallite length, and it has been observed that results from different sources do not show good agreement. However, two sets of self-consistent results [13] (also B. M. King, personal communication), when separately compared with the estimate of crystallite cross-section given here (Table III), suggest that there is a rough correlation between crystallite length and crystallite width or thickness. Those fibres having lower accessibilities and fewer crystallites of large cross-section, such as Fortisan and Fibre G, also exhibit high levelling-off degrees of polymerisation, which have been interpreted as an index of crystallite length.

Other interpretations of the results of accessibility determinations have been made by Mark [2] and Howsmon [3]. These workers assigned an average crystallite size, estimated from X-ray determination and electron-microscopic measurements on hydrolysed celluloses, to a series of fibres, and then interpreted the differences of accessibility

in terms of different total crystallinities. In view of the uncertainty attending such methods of estimating crystallite size at present, this procedure is not wholly satisfactory.

Kast [1] has used a method of interpretation similar to that adopted here, taking X-ray crystallinity data for one series of fibres from Hermans [10] and deuterium oxide accessibilities for another (similar) series of fibres from Mark [2]. His results, which relate to native fibres and two samples of regenerated cellulose, show features similar to those presented here.

Valentine [27] has related sorption ratio to the fraction of amorphous material as determined by Mann and Marrinan [4], and shows that the relation is linear for four cellulose samples. This relation seems to be unsupported, for it is clear that the sorption ratio, determined from equilibrium sorption regain measurements, is related to accessibility (i.e. to equilibrium deuterium exchange) and not to the fraction of amorphous material. The results given in Table III provide no support for the relation proposed by Valentine.

4. SOME GENERAL CONSIDERATIONS

It has already been observed (Table III) that the accessibilities and crystallinities of the fibres examined seem to be linked with their methods of spinning. Thus fibres to which a high stretch is applied whilst they are still in a highly swollen condition, such as Fibre G, ammonium-sulphate-spun yarn, and Durafil, possess low accessibilities and high crystallinities. Conversely, fibres which are known to exhibit a low degree of swelling in their freshly formed state before the deliberate application of stretch, such as the Tenasco high-tenacity yarns, possess lower crystallinities.

The former group of fibres are highly swollen either as a result of the presence within the fibre at the time of stretching of many bulky and hydrophilic xanthate groups (Fibre G, ammonium-sulphate-spun yarns) or as a result of the swelling and plasticising action of the spinning solution (Durafil). The deliberate application of a high degree of stretch to such fibres leads to the cellulose chains taking up highly oriented positions favourable to the formation of both higher total crystallinity and larger crystallites.

In the case of the other group of fibres, regeneration to cellulose is nearly complete before the orienting forces are applied. Moreover, the high concentration of zinc ions employed in the spinning of such fibres is thought to produce a gel thread in which the meagrely xanthated cellulose chain segments possess restricted mobility. Certainly, gels of zinc cellulose xanthate have a lower degree of swelling than those of sodium or ammonium cellulose xanthate, and yet are capable of being subjected without rupture to a higher degree of rapidly applied stretch. The ability to undergo rapid extension without rupture is of considerable practical importance, for the rate of application of stretch in an industrial process is in fact governed by the elastic and work-hardening characteristics of the fibre. Thus it is common practice to apply stretch between two wheels or rollers rotating at different speeds. The distance apart of such devices, however, does not determine the distance over which the stretch is applied, and frequently the majority of the stretch applied takes effect over a very short distance. It is thought that in the case of these fibres, a limited number of xanthate groups are associated with a stoichiometric number of zinc ions in the form of an ionic complex that is more stable to decomposition by hydrogen ions than is sodium cellulose xanthate. In such a structure the tendency of cellulose chain segments to rotate into positions favourable to extensive random crystallisation will be restricted. Hence, during the extension and regeneration to cellulose which occur when such a fibre is stretched in hot water or hot dilute acid, many crystal nuclei will be formed, and the final structure, although fairly highly oriented, will be one composed of numerous small regions of high order.

TABLE VII

Water of Imbibition and Skin–Core Appearance of some Cellulose Fibres regenerated from Viscose

Fibre	Average Crystallite Size (A.G.U. in side)	Water of Imbibition (%)	Skin–Core Description
Spun into bath containing ammonium sulphate	4·8	105–110	No skin
Textile rayon ...	4·3	95–100	Thin skin
Tenasco high-tenacity rayon	3·9	80–90	Thick skin
Tenasco 35 ...	3·1	70–75	Very thick skin
Tenasco Super 70	$\geq$ 2·5	65–70	All skin

General considerations would lead one to expect that the presence within a cellulose fibre of large crystallites and therefore large amorphous regions would be undesirable. Such a structure would tend to behave as a two-phase system, and the larger the crystallites the less chance there would be of a single cellulose chain passing through a given number of crystallites, at a given degree of polymerisation. A structure composed of smaller crystallites, occurring more frequently, may be regarded as providing a more homogeneous fine structure. This is particularly so in the wet state, for a network of many water-resistant crystallites will restrict swelling and thus possess improved physical properties in the wet state. Clearly, these remarks apply particularly to two fibres having similar total crystallinity, but the argument is valid for fibres having crystallinities which are not too dissimilar. Table VII gives the values of water of imbibition for a selection of the fibres listed in Table III. It will be seen that it is just those fibres which have high accessibilities and similar total crystallinities which possess low water imbibitions. It is to be expected that a structure containing many small crystalline regions would exhibit lower lateral swelling in water, and as stated, this seems to be so. This may be regarded as further qualitative support for the interpretation given here of the accessibility results. However, since these fibres possess, by virtue of their finer crystalline texture, higher accessibilities, it follows that at some point the sorption isotherm of such

fibres should cross those of fibres possessing a coarser crystalline texture. As noted earlier, the method employed here for the determination of sorption isotherms is not suitable at relative humidities above about 80%. It seems likely that the cross-over points, which must exist, will occur at relative humidities greater than 95%.

The use of water of imbibition as a qualitative indication of change in fine structure is valid only when the fibres being compared have similar orientation (particularly orientation of the non-crystalline portion). High orientation of the whole fibre substance of the type found in Durafil, for example, can also lead to low water of imbibition, as, of course, can higher total crystallinity.

It appears from Table III that there is a correlation in some cases between high orientation, high crystallinity, and low accessibility. For a series of fibres spun by the same regenerative spinning process Howsmon [28] has shown that there is a slight decrease in accessibility with increasing orientation. In the course of experiments reported here this was confirmed, and it was also found that there was a slight increase in crystallinity (density) with increase in orientation. The order of these changes was small compared with the range of accessibilities and crystallinities quoted in Table III, and it seems clear that the nature of the regenerative spinning process and not orientation itself is responsible for the major changes in the level of crystallinity and accessibility. Thus orientation is only one of many factors in a process leading to the formation of a regenerated cellulose fibre which influences the structural arrangement.

The heterogeneous nature of some viscose rayons was first noted in 1931, when Preston [29] reported the presence of an outer layer, or skin, surrounding a central core. Since that date many different types of viscose rayon fibre have been developed showing differences, *inter alia*, in the relative proportions of skin and core.

The definition and delineation of skin and core, as shown, for instance, by the differential staining test of Morehead and Sisson [5], are to some extent arbitrary. The two are not separate and unique entities. It is probable that a range of crystallite sizes exists in each, and that other factors, such as molecular alignment in the amorphous regions, influence the staining behaviour. However, it should be noted that the size of these regions is not, as has sometimes been suggested, determined by the dye used for their identification, for the boundary between skin and core may be demonstrated by mounting cross-sections in water. Again, it has been shown by the use of the interference microscope that there is a real and sharp change in the optical properties at this boundary.

In spite of the reality of the boundary between two different types of cellulose substances, regarded as skin and core, the nature of the difference has remained obscure. Thus, the suggestion that the difference is due to differences in orientation was untenable, for isotropic films showing the skin–core effect can be prepared [30, 31]. The skin–core character of a number of viscose rayons is indicated in Table VII. Clearly, there is a relation between the average crystallite size estimated from accessibility and crystallinity determinations and the proportion of skin possessed by a given fibre: the greater the proportion of skin, the smaller is the average crystallite size. In view of the arbitary nature of the skin–core differential staining test, however, it is probably justifiable only to relate fibres of a given type, e.g. prepared under a given set of spinning conditions, in this way.

It was suggested above that the cellulose fibre composed of very small crystallites would exhibit better properties in the wet state than one composed of fewer larger crystallites. In fact it has been found that the viscose rayons possessing thicker skins exhibit better all-round properties than the earlier, thin-skinned fibres. Thus, as the proportion of skin increases, the water of imbibition and the cross-sectional swelling in water are lower, the degree of orientation obtainable for a given applied extension during spinning is greater, the ratio of wet: dry tenacity is increased, and the work to rupture is increased.

Thus it appears that the division between skin and core in a given series of viscose rayon fibres, related as it is to difference in average crystallite size, is a useful practical guide to the properties of such fibres.

On the microscopic scale, as distinct from the macroscopic, it is known that in some cases the skin–core boundary can develop into a fault, or microcapillary, extending lengthways in the fibre. Clearly, elimination of this source of weakness by the preparation of fibres having no skin–core boundary is of practical importance.

This investigation has demonstrated that differences of crystallinity and average crystallite size exist among the different viscose rayon fibres, and it has been shown that there exists a qualitative relationship between such differences, the properties of such fibres, and the nature of the regenerative spinning process. It is considered, however, that this simple picture must be modified to take account of differences in the distribution of lateral order, both amongst different fibres and across a given fibre, before a more quantitative approach to the relation between fibre structure and properties can be contemplated. No satisfactory techniques for such investigations have yet been reported.

* * *

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The Chemistry of Esters of Leuco Vat Dyes

III—The Oxidation of the Mono- and Di-sulphuric Esters of Quinol (Hydroquinone) and of 1:4-Naphthaquinol with Acidic Hydrogen Peroxide

A. JOHNSON and M. L. RAHMAN

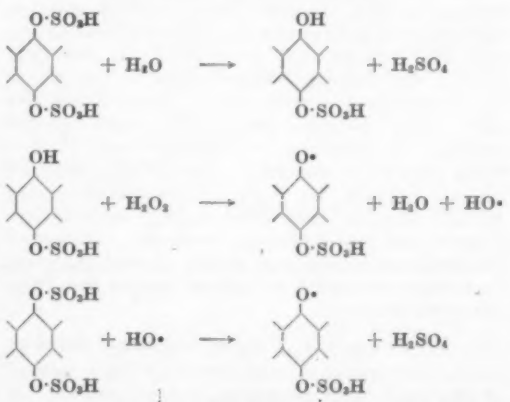
The mono- and di-sulphuric esters of 1:4-naphthaquinol react with acidic hydrogen peroxide in the same way as the di-sulphuric ester of 9:10-anthraquinol-2-sulphonic acid: i.e. removal of most of the sulphate groups by direct oxidation follows removal of some groups by hydrolysis. The catalytic effect of the mono-ester in the oxidation of the di-ester has been directly demonstrated. On the other hand, with the mono- and di-sulphuric esters of quinol, the sulphate groups are not removed by direct oxidation but by hydrolysis only. Oxidation of the resultant quinol then follows as a separate reaction.

Introduction

In Part I [1] the behaviour of the disulphuric ester* of 9:10-anthraquinol-2-sulphonic acid towards acidic hydrogen peroxide was examined in some detail. It was concluded that the overall reaction is complicated and consists of a number of steps. The first of these was thought to be a slow hydrolysis of part of the di-ester to give the mono-ester. The small concentration of mono-ester thus produced then reacted with hydrogen peroxide to produce a semiquinone ester and a hydroxyl radical. Subsequent reactions of the hydroxyl radical depended on the experimental conditions, particularly the concentration of hydrogen peroxide. The radical could react either directly with a molecule of the diester, or with hydrogen peroxide to form other active oxidising species, which in turn could react with the di-ester. Either case resulted in a considerable part of the di-ester being oxidised directly, to a semiquinone ester, without any need to be first hydrolysed. Some of these reactions are indicated below.

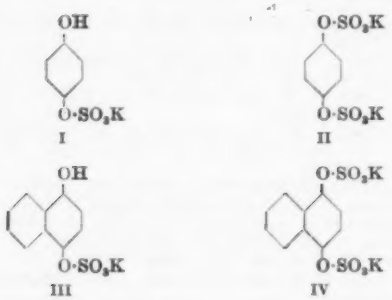
The results of oxidising a large number of purified commercial vat esters [2] of the indigoid series were in agreement with the above conclusions.

* The disulphuric esters of quinols and leuco vat dyes will be referred to generically as *vat esters*.



As a result of this work, it seemed of interest to examine esters other than anthraquinonoid or indigoid derivatives, and in particular to study the behaviour of monosulphuric esters of quinols, since these have an important rôle in the suggested scheme of reactions.

Accordingly, four sulphuric esters, two each from the benzene and naphthalene series, have been studied. These are potassium salts of 4-hydroxyphenyl sulphate (I), 1:4-phenylene disulphate (II), 4-hydroxy-1-naphthyl sulphate (III), and 1:4-naphthylene disulphate (IV).



Each of these esters in turn was treated with hydrogen peroxide in solutions of hydrochloric acid, *in vacuo* and in the dark. The reaction with solutions of hydrochloric acid only was studied also. The course of the reactions was followed, as in the previous work, by measuring the rates of liberation of sulphate and of consumption of hydrogen peroxide. In addition to measurements on the four compounds separately, the effect of additions of 4-hydroxy-1-naphthyl sulphate (III) on the oxidation of 1:4-naphthylene disulphate (IV) was also studied.

Experimental

MATERIALS

(*i*) *Potassium Salt of 1:4-Phenylene Disulphate*

A solution of quinol (hydroquinone, 20 g.) in pyridine (100 ml.) was added slowly with stirring to pyridine–sulphuric anhydride made from chlorosulphonic acid (30 ml.) and pure pyridine (80 ml.), at a temperature below 40°C. The temperature was then raised to 65°C. during 1 hr. and maintained at this value for a further hour. After cooling to 50°C., a concentrated aqueous solution containing 52 g. of potassium hydroxide was added, and the mixture left overnight. It was then filtered, and sufficient ethanol added to the filtrate to precipitate the crude ester. Purification was effected by fractional precipitation from aqueous solution by additions of ethanol, each fraction being tested for chloride, inorganic sulphate, and organic sulphate, i.e. the ester (precipitation with barium chloride only after boiling with hydrochloric acid and hydrogen peroxide). Repeated fractionation in this way finally yielded the ester as a colourless, finely crystalline powder free from inorganic ions.

(*ii*) *Potassium Salt of 4-Hydroxyphenyl Sulphate*

This was prepared from phenol by Elb's method of oxidation with potassium persulphate[3,4]. A solution of potassium persulphate (18 g.) in 200 ml. of water was added, over a period of 3 hr., to phenol (6 g.) dissolved in a solution of potassium hydroxide (18 g.) in 200 ml. of water, the temperature being maintained below 15°C. The following day the resultant dark brown mixture was made just acid to Congo Red (C.I. Direct Red 28), and unchanged phenol extracted with ether. Addition of ethanol to the aqueous phase caused precipitation of potassium sulphate, and after filtration and clarification with charcoal the filtrate was evaporated to dryness *in vacuo* at 40°C. The residue of crude ester was purified by extraction with ethanol followed by fractional precipitation with ether, the fractions being tested for chloride, inorganic sulphate, and organic sulphate. Repeated fractionation yielded the ester as very fine, white crystals.

(*iii*) *Potassium Salt of 1:4-Naphthylene Disulphate*

An intimate mixture of 1:4-naphthaquinone (10 g.) and copper powder (4 g.) was slowly added with stirring to pyridine–sulphuric anhydride made from chlorosulphonic acid (17 ml.) and pure pyridine (56 ml.), at a temperature below 20°C. The temperature was then raised to 75°C. in 30 min., and maintained at this value for 90 min. After cooling to 30°C., 200 ml. of a solution containing 14 g. of potassium carbonate was added, the mixture left overnight, then a concentrated solution of potassium hydroxide (27 g.) added, and the mixture heated at 40°C. for 15 min. The resultant precipitate of copper oxide was removed, and inorganic salts were further precipitated from the filtrate by adding ethanol, after which the filtrate was evaporated to dryness at 40°C. *in vacuo*. The residue of crude ester was purified by extraction with an acetone–ethanol mixture (3 : 2 by vol.) followed by careful precipitation with chloroform. It was finally obtained as a fine, off-white powder.

(*iv*) *Potassium Salt of 4-Hydroxy-1-naphthyl Sulphate*

This was prepared from 1-naphthol (7·2 g.) and potassium persulphate (13·5 g.) by the same method as the salt of 4-hydroxyphenyl sulphate (*ii*). The temperature was kept at 0°C. during the addition of the persulphate, and after ether extraction of unchanged 1-naphthol the aqueous solution was evaporated to dryness at 40°C. *in vacuo*. The residue thus obtained was purified by repeated extraction with ethanol followed by precipitation from the extract by means of ether.

The esters were shown to be pure by oxidising in boiling 2 N. hydrochloric acid containing an excess of hydrogen peroxide, for 2 hr. Sulphate liberated was then measured colorimetrically, and was always found to be more than 96% of theoretical.

(*v*) *Other Materials*

All other materials were of AnalaR quality.

MEASUREMENT OF RATES OF REACTION

The rates of hydrolysis and oxidation with hydrogen peroxide of the four esters were measured at 45°C. *in vacuo* and in the dark using the apparatus described in Part I[1]. Samples of the reaction solutions were withdrawn from time to time and analysed for sulphate and hydrogen peroxide using the colorimetric methods of Ainsworth and Johnson[1] and of Ovenston and Rees[5] respectively, which are described in detail in Part I.

Results

1. BENZENE DERIVATIVES

The results of experiments with the two phenyl esters are shown in Fig. 1, where moles of sulphate

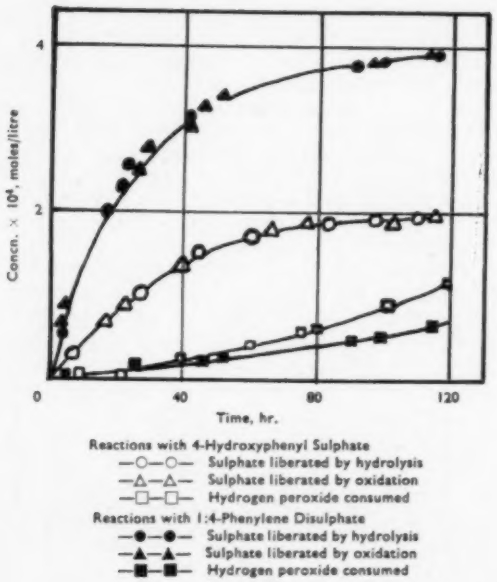

Concn. × 10⁴, moles/litre
Time, hr.
Reactions with 4-Hydroxyphenyl Sulphate
—○—○— Sulphate liberated by hydrolysis
—△—△— Sulphate liberated by oxidation
—□—□— Hydrogen peroxide consumed
Reactions with 1:4-Phenylene Disulphate
—●—●— Sulphate liberated by hydrolysis
—▲—▲— Sulphate liberated by oxidation
—■—■— Hydrogen peroxide consumed

FIG. 1

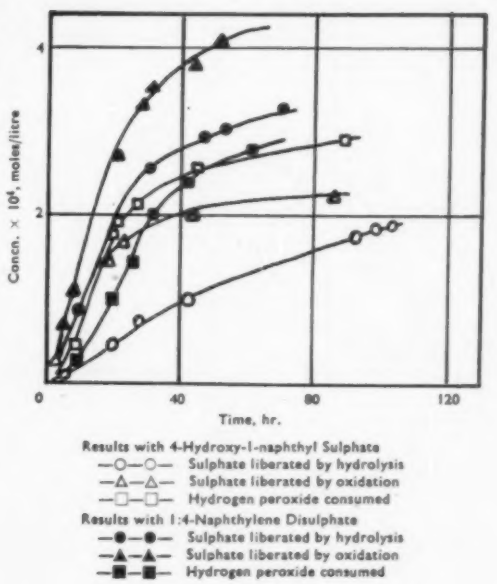

Concn. × 10⁴, moles/litre
Time, hr.
Results with 4-Hydroxy-1-naphthyl Sulphate
—○—○— Sulphate liberated by hydrolysis
—△—△— Sulphate liberated by oxidation
—□—□— Hydrogen peroxide consumed
Results with 1:4-Naphthylene Disulphate
—●—●— Sulphate liberated by hydrolysis
—▲—▲— Sulphate liberated by oxidation
—■—■— Hydrogen peroxide consumed

FIG. 2

liberated and hydrogen peroxide consumed are plotted against time. In each case the initial concentration of the ester was $2{\cdot}5 \times 10^{-4}$ M. and that of hydrochloric acid 0·285 N. In the oxidation experiments the initial concentration of hydrogen peroxide was also $2{\cdot}5 \times 10^{-4}$ M., i.e. equivalent to the ester. It will be seen that, for each ester, sulphate is liberated at the same rate by both hydrolysis and oxidation. In the oxidation experiments the initial rate of consumption of peroxide is much lower than the rate of liberation of sulphate, but increases with time. Sulphate is liberated much more rapidly from the di-ester than from the mono-ester, but hydrogen peroxide is consumed rather more slowly.

2. NAPHTHALENE DERIVATIVES

The two naphthalene esters were hydrolysed and oxidised under the same conditions as the benzene derivatives (see § 1 above), with the results shown in Fig. 2. In both cases, sulphate is liberated far more rapidly by oxidation than by hydrolysis. This is markedly different from the behaviour of the benzene derivatives, as also is the consumption of hydrogen peroxide, which in the latter part of the reaction exceeds the amount of sulphate liberated (it should be borne in mind that for the di-ester $H_2O_2 \equiv 2H_2SO_4$). The results with the naphthalene derivatives are, in fact, typical of those previously obtained for a number of vat esters[1,2], whilst those of the benzene derivatives are not. The naphthalene compounds were, therefore, examined in detail.

In these further experiments the initial concentration of the esters was kept constant at $2{\cdot}5 \times 10^{-4}$ M., and hydrochloric acid was used at three concentrations—0·5 N., 0·25 N., and 0·1 N. A hydrolysis experiment was performed at each acid concentration, and was followed by oxidation experiments using 10^{-3} M., $2{\cdot}5 \times 10^{-4}$ M., and $1{\cdot}0 \times 10^{-4}$ M. hydrogen peroxide. In order to maintain activity coefficients constant[6], the ionic strength was adjusted to 0·75 by the appropriate addition of potassium chloride. This also ensured that the chloride ion concentration remained constant at 0·75 g.-ion per litre.

(i) *Results with Potassium Salt of 4-Hydroxy-1-naphthyl Sulphate*

In hydrolysis experiments, i.e. with no added hydrogen peroxide, the rate of liberation of sulphate increased with increasing concentration of hydrochloric acid. Plots of $\log(a - x)$ against time, where a = initial concentration of ester and x = amount decomposed at time t (equivalent to the concentration of liberated sulphate), were linear; i.e. the reaction is of the first order with respect to the ester. The first-order rate constants

TABLE I

Rate Constants for 4-Hydroxy-1-naphthyl Sulphate*

[HCl] (N.)	$10^4[H_2O_2]$ (M.)	10^5k_1 (hr.$^{-1}$)	10^5k_2 (hr.$^{-1}$. moles^{-1} litre)	$10^5k_1'$ (hr.$^{-1}$)
0·5	0	0·228	0·045	
	10·0	0·398		0·170
	2·5	0·362		0·134
	1·0	0·271		0·043
0·25	0	0·097	0·039	
	10·0	0·260		0·163
	2·5	0·232		0·135
	1·0	0·130		0·033
0·1	0	0·046	0·046	
	10·0	0·198		0·152
	2·5	0·143		0·097

* k_1 = Observed first-order constants for hydrolysis and oxidation experiments.
k_2 = Derived bimolecular constant for hydrolysis.
k_1' = k_1 oxidation − k_1 hydrolysis at the same acid concentration = First-order constant for oxidation only.

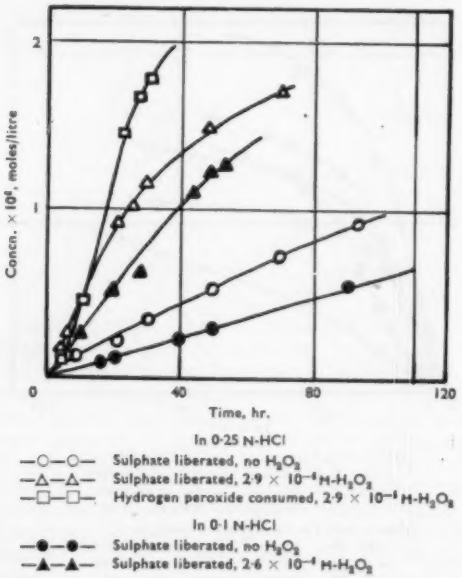

Concn. × 10⁴, moles/litre
Time, hr.
In 0·25 N-HCl
Sulphate liberated, no H_2O_2
Sulphate liberated, 2·9 × 10^{-4} M-H_2O_2
Hydrogen peroxide consumed, 2·9 × 10^{-4} M-H_2O_2
In 0·1 N-HCl
Sulphate liberated, no H_2O_2
Sulphate liberated, 2·6 × 10^{-4} M-H_2O_2

FIG. 3— Reactions with 4-Hydroxy-1-naphthyl Sulphate

k_1 and the corresponding derived bimolecular constant k_2 are given in Table I, showing that the rate of hydrolysis is directly proportional to the concentration of hydrolysing acid, in accordance with the results of Burkhardt *et al.*[7].

The addition of hydrogen peroxide causes a marked increase in the rate of liberation of sulphate, the rate increasing with increasing concentration of hydrogen peroxide. The effect of hydrogen peroxide is greatest at the lowest acid concentration. Typical curves are shown in Fig. 3. In these experiments, sulphate is being liberated by both hydrolysis and oxidation, so that a simple rate equation is not likely to be applicable to the whole course of the reaction. Nevertheless, plots of log $(a - x)$ against time were linear for about the first 35% of the reactions, so that first-order rate constants k_1 for this region could be obtained. These are included in Table I. Also included are values of k_1', obtained by subtracting from k_1 for an oxidation experiment the value of k_1 for the corresponding hydrolysis experiment. The values of k_1' are seen to be reasonably independent of acid concentration, except when the concentrations of both acid and peroxide are low. This suggests that two distinct reactions, hydrolysis and oxidation, are taking place, k_1' being the first-order rate constant for the oxidation reaction only.

Measurement of hydrogen peroxide concentrations showed that, except for the early part of the reaction, the amount of peroxide consumed exceeded the sulphate liberated, and could, in fact, exceed the theoretical amount of peroxide needed for complete oxidation of the whole of the ester when the peroxide concentration was sufficiently high. This can only mean that hydrogen peroxide may be consumed in a side-reaction. At the beginning of an experiment the consumption of peroxide lags behind the liberation of sulphate (Fig. 3).

(*ii*) *Results with Potassium Salt of 1:4-Naphthylene Disulphate*

This compound was hydrolysed and oxidised under the same conditions as the mono-ester, and showed the same qualitative behaviour. The rate of hydrolysis, as measured by sulphate determination, increases with increasing concentration of acid; sulphate liberation is accelerated by the addition of hydrogen peroxide, and the effect of hydrogen peroxide is most marked at lower acid concentrations. Again, the consumption of peroxide in the early stages lags behind the liberation of sulphate, but ultimately exceeds it and may exceed the theoretical value. A selection of the results is shown in Fig. 4.

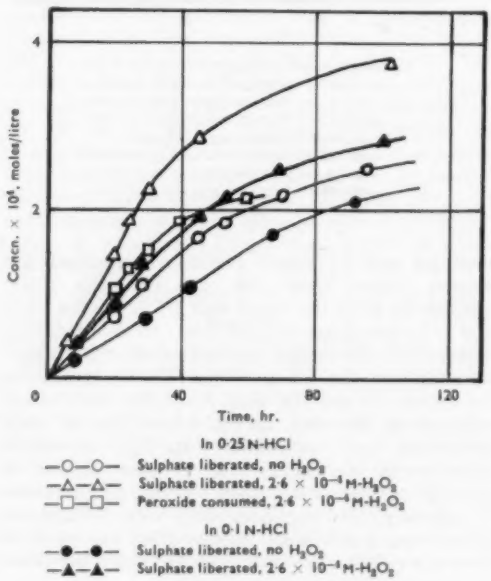

Concn. × 10⁴, moles/litre
Time, hr.
In 0·25 N-HCl
Sulphate liberated, no H_2O_2
Sulphate liberated, 2·6 × 10^{-4} M-H_2O_2
Peroxide consumed, 2·6 × 10^{-4} M-H_2O_2
In 0·1 N-HCl
Sulphate liberated, no H_2O_2
Sulphate liberated, 2·6 × 10^{-4} M-H_2O_2

FIG. 4— Reactions with 1:4-Naphthylene Disulphate

Since the two sulphate groups are not lost at the same rate, it is not possible, in this case, to equate liberated sulphate with reacted vat ester, and so significant rate constants cannot be obtained.

(*iii*) *Effect of Alkali on partly Reacted Esters*

In the oxidation of the vat ester of anthraquinone-2-sulphonic acid, it was observed that additional sulphate could be removed from the partly oxidised ester if the acidic solution were made alkaline. This was ascribed to the existence of a semiquinone ester. Similar observations were made with both mono- and di-esters of naphthaquinol, so that the existence of a semiquinone ester must be assumed here also. For this determination a suitable aliquot of reaction solution was added to a known volume of potassium hydroxide solution (in excess). After standing for 5 min. the solution was again made acidic with hydrochloric acid, and and sulphate analysis proceeded with in the usual way. Some of the results are shown in Fig. 5.

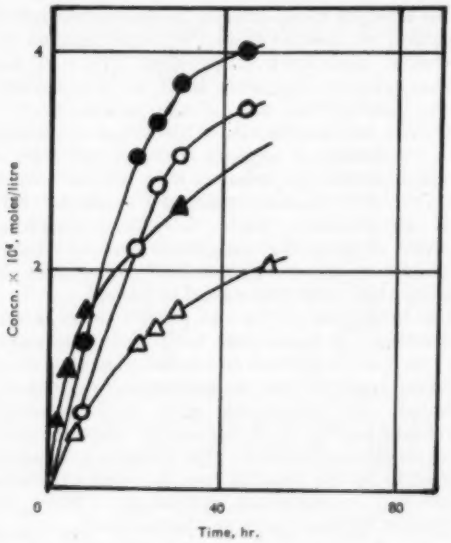

Concn. × 10⁴, moles/litre
Time, hr.
1:4-Naphthylene Disulphate in 0·5 N-HCl, 2·7 × 10⁻⁴ M-H₂O₂
—○—○— Sulphate liberated in acidic soln.
—●—●— Sulphate after making alkaline
4-Hydroxy-1-naphthyl Sulphate in 0·25 N-HCl, 1·0 × 10⁻⁴ M-H₂O₂
—△—△— Sulphate liberated in acidic soln.
—▲—▲— Sulphate after making alkaline

FIG. 5— Effect of Alkali on Sulphate Liberation from Naphthyl Esters

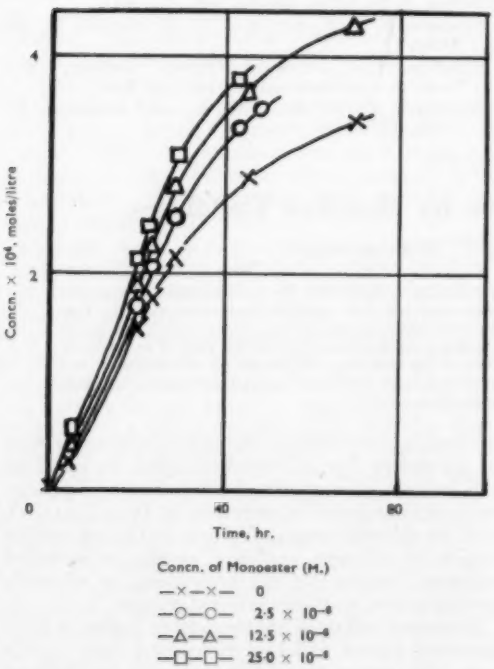


FIG. 6— Effect of 4-Hydroxy-1-naphthyl Sulphate on Oxidation of 1:4-Naphthylene Disulphate in 0·25 N-HCl + 2·5 × 10⁻⁴ M-H_2O_2

(iv) Effect of Added 4-Hydroxy-1-naphthyl Sulphate on the Oxidation of 1:4-Naphthylene Disulphate

The mono-ester was added to solutions of the di-ester ($2{\cdot}5 \times 10^{-4}$ M.) in hydrogen peroxide ($2{\cdot}5 \times 10^{-4}$ M.) at the three concentrations of hydrochloric acid used before. The concentration of mono-ester was 1, 5, or 10 molar % of the di-ester concentration.

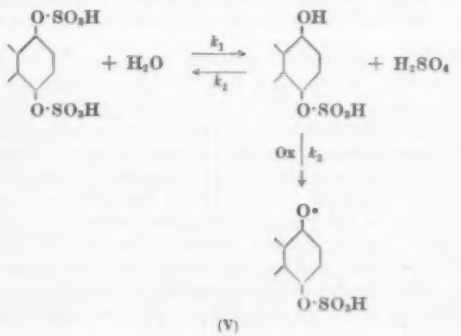
Some results are shown in Fig. 6, where it will be seen that the presence of mono-ester causes an increase in the rate of liberation of sulphate from the di-ester, the effect being greater at lower acid concentrations. Consumption of hydrogen peroxide follows the same lines as before. It should be noted that the increased sulphate produced cannot be accounted for solely by decomposition of the mono-ester, since the increase in sulphate is greater than the amount of mono-ester taken.

Discussion

In Part I [1] a mechanism of development of the vat ester of anthraquinone-2-sulphonic acid was proposed, the important steps of which are given on p. 291. According to this the mono-ester, produced by irreversible hydrolysis of the di-ester, is oxidised to the semiquinone ester by means of molecular hydrogen peroxide and at the same time produces other oxidising radicals which are capable of directly oxidising further molecules of di-ester to semiquinone ester. Similar reactions with the second ester group, i.e. reactions of the mono-ester and semiquinone ester, must also be possible, but were not very pronounced with the anthracene derivative.

In the present work, the results for the two naphthalene derivatives fit in with this type of mechanism. The rate of removal of sulphate groups by oxidation is always greater than by hydrolysis alone. If the hydrolysis reaction is irreversible, it follows that some of the sulphate groups must be removed by direct oxidation— without specifying the nature of the oxidising entity.

An alternative to this theory is to propose that the hydrolysis reaction leading to the formation of sulphate, or at least one stage of it, is reversible. If an oxidising agent is now added, the hydroxy compound produced by hydrolysis— presumably the mono-ester— will be removed by oxidation, so that the hydrolysis equilibrium will be shifted, and the rate of formation of sulphate increased—



(V)

The results with the two benzene derivatives, however, do not support this suggestion. Although, in this case, the esters are completely hydrolysed to quinol, which is then oxidised, the hydrolysis must be irreversible, since the addition of hydrogen peroxide has no effect on the rate of formation of sulphate.

It is not reasonable to assume that the naphthyl esters are hydrolysed in any way differently from the phenyl esters. In fact the kinetics of the naphthyl mono-ester hydrolysis are in agreement with those found by Burkhardt *et al.*[7] for a number of phenyl esters. So it must be assumed that hydrolysis of the naphthyl esters is not reversible, and that the increase in rate due to hydrogen peroxide is caused by direct oxidation of the ester groups.

Further evidence for the mechanism put forward in Part I[1] is to be found in the effect of the naphthyl mono-ester on the oxidation of the di-ester. A marked increase in rate is observed (Fig. 6), in agreement with the suggestion that the mono-ester initiates direct oxidation of the di-ester.

However, it must be remembered that the mono-ester can be hydrolysed further to the quinol, which is also known to increase the rate of oxidation of the vat ester of anthraquinone-2-sulphonic acid[1]. It is not possible to decide which of the two species, mono-ester or quinol, or both of them, is the active oxidation initiator. Some of the results with the naphthyl esters suggest that complete hydrolysis of part of the ester to the quinol is necessary before oxidation can be initiated. Thus, the consumption of peroxide always lags behind the liberation of sulphate in the early part of the reaction. However, hydrolysis of the ester groups in both of the naphthalene compounds occurs much more rapidly than with the vat ester of anthraquinone-2-sulphonic acid, so that, although some quinol may be formed and initiate oxidation in the naphthalene series, it is much less likely in the anthracene series.

The effect of mono-ester of increasing the rate of oxidation of di-ester is also evidence against the reversible hydrolysis mechanism (V). If this mechanism were applicable, additions of mono-ester would increase the rate of the reverse reaction and hence decrease the rate of liberation of sulphate.

In conclusion, it appears that the vat ester of 1:4-naphthaquinone behaves in a similar way to the vat ester of anthraquinone-2-sulphonic acid. The experiments with 4-hydroxy-1-naphthyl sulphate support the suggestion that the mono-ester acts as an oxidation initiator, but it is also possible that some free quinol is formed.

The behaviour of the two phenyl esters is very interesting. It seems that both these compounds are much more difficult to oxidise than the corresponding naphthalene or anthracene derivatives, although, in agreement with the arguments developed in Part II of this series[2], they are much more readily hydrolysed. The benzene compounds appear to be the limiting case in which hydrolysis completely overwhelms oxidation. They are worthy of further study on that account.

* * *

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Adsorption of a Reactive Dye by Modified Celluloses

E. H. DARUWALLA and P. SUBRAMANIAM

The equilibrium adsorption of commercial Procion Brilliant Red 2BS by acid-modified cellulosic fibres and by standard cellulose altered by the specific action of different oxidising agents is studied. The equilibrium adsorption by all the fibres decreases rapidly in the initial stages of the action of acid, but tends to level off with further hydrolysis. The extent of the decrease depends mainly on the rate of removal of the hydrolysable fraction and the extent of crystallisation of the cellulose chains during the action of the acid. The reduction in dye uptake is more marked when primary alcoholic groups are converted into carboxyls than when secondary alcoholic groups are similarly oxidised.

Of late considerable interest has been shown in the dyeing of cellulosic fibres with reactive dyes such as the Procions (ICI) and Cibacrons (Ciba). The fibre–dye attachment in the case of dyes belonging to these ranges has been mainly attributed to chemical bonding between suitable groups in the dye molecule and hydroxyl groups in the cellulose fibre substance[1]. At present, no quantitative data are available for the uptake of these dyes by different cellulosic fibres and for the changes in dye adsorption with changes in the accessible hydroxyl groups present in the fibre substance. The present work is a preliminary study of the equilibrium adsorption of a reactive dye by modified celluloses in which the fraction of accessible hydroxyl groups present in the fine structure is altered by (1) the action of an acid on different cellulosic fibres or (2) the specific action of different oxidising agents on standard cellulose, leading to the conversion of alcoholic groups to non-reacting carboxyl groups.

Standard cellulose prepared from Indian cotton, standard cotton cellulose mercerised with caustic soda (25% concn. by wt.) at 15°C. with and without the application of tension, and cuprammonium

TABLE I

Equilibrium Adsorption of Procion Brilliant Red 2BS by Acid-modified Celluloses

Loss in Weight during Hydrolysis (%)	Procion Brilliant Red 2BS on Fibre (g./kg. bone-dry fibre)			
	Standard Cellulose	Cellulose mercerised		Cuprammonium Rayon
		Under tension	Without tension	
Nil	26·8	49·9	62·8	97·8
0·7	23·8	31·9	49·4	71·9
1·0	22·5	27·5	43·1	63·8
1·8	20·0	21·9	30·0	52·5
2·4	17·8	20·0	24·4	48·7
3·5	15·0	18·6	22·5	43·1
4·2	13·8	18·5	21·8	40·8
5·2	12·8	17·9	21·5	38·8
6·5	12·5	17·7	21·5	38·5
7·3	12·5	17·5	21·2	38·5
8·8	12·5	17·5	21·2	38·5

rayon were used as fibre substances. Hydrocelluloses from these fibres were prepared by steeping the fibres in 7 N. sulphuric acid at 30 ± 1°C. for different periods (4–900 hr.), keeping the liquor ratio at 50 : 1. After hydrolysis the samples were washed free from acid with distilled water, air-dried, and brought to equilibrium moisture content at 65% R.H. and 30°C. Percentage loss in weight sustained by the fibre substance during various stages of hydrolysis was calculated on the original sample on a bone-dry basis. The moisture regain for each hydrocellulose was arrived at by conditioning the sample to equilibrium over a suitable desiccant. Periodate–chlorite-treated oxycelluloses were prepared from standard cellulose by first treating the fibre substance with 0·01 M. potassium metaperiodate for different periods at 30°C. with a liquor ratio of 50 : 1, washing with distilled water till free from periodate, air-drying, and subsequently treating with a solution of chlorous acid 0·1 M. with respect to sodium chlorite and 0·5 M. with respect to phosphoric acid at 30°C. for 18 hr., washing, and drying at 30°C. Dichromate–oxalic acid oxycelluloses were prepared by the method suggested by Clibbens and Ridge [2]. These oxycelluloses were given the same standard chlorous acid treatment as the periodate oxycelluloses. The carboxyl contents of both types were determined iodometrically [3].

Dyeings were carried out with commercial Procion Brilliant Red 2BS (ICI) without purification, because a method for its purification is not available at present. Samples were dyed at 27 ± 1°C. in a suitable apparatus provided with a stirring arrangement, from a bath containing 1 g. dye and 30 g. sodium chloride per litre, and dyeing was carried on for 30 min. Anhydrous sodium carbonate (1 g./litre) was then added to the dye-bath, and dyeing was continued till equilibrium was attained. The dyed sample was washed completely free from the loosely held dye, and conditioned at 65% R.H. and 30°C. A known weight of the dyed sample was dissolved in 19 N. sulphuric acid at 10°C., and the amount of dye taken up by the fibre was estimated colorimetrically on the Hilger Spekker absorptiometer, which had been previously calibrated with standard solutions of the Procion dye in 19 N. sulphuric acid.

Results are expressed in terms of grams of commercial dye on the fibre per kilogram of bone-dry sample. In Table I are given values of the equilibrium dye uptake for different cellulosic fibres and for hydrocelluloses produced from them by the progressive action of acid. Fig. 1 represents values of moisture regain ratios—

$$\frac{\text{Moisture regained by hydrocellulose (\%)}}{\text{Moisture regained by unhydrolysed sample (\%)}}$$

plotted against corresponding ratios for dye uptake for hydrocelluloses prepared from different cellulosic fibres. Results for the dye uptake by different oxycelluloses are plotted in Fig. 2.

The results in Table I indicate that, under identical conditions of dyeing, the dye uptake increases in the order— standard cellulose < cellulose mercerised under tension < cellulose mercerised without tension < cuprammonium rayon. This is in agreement with the proportion of non-crystalline regions present in the respective fibre substances [4] and the availability of hydroxyl groups for combination with the dye molecule. With all the fibres studied, under identical conditions of acid action, the dye uptake decreases appreciably during the initial stages, less so during the second stages, and in the final phase of hydrolysis there is a tendency for the uptake to remain constant. This behaviour can be explained by assuming that changes in the fine structure of cellulose take place during progressive mild hydrolysis. During the initial stages of mild acid action, a random breakdown of the 1:4-glucosidic linkages in the cellulose chain molecules present in the non-crystalline regions takes place, and an appreciable fraction of the readily accessible region is dissolved off in the aqueous acidic medium. Simultaneously the fine structure of cellulose undergoes crystallisation, as evidenced by a definite increase in the crystalline fraction of the fibre substance [5]. The accessibility of the hydroxyl groups is a function of the proportion of non-crystalline regions present and the degree of orientation of cellulose chains. The removal of the hydrolysable portion as well as the crystallisation of fringed chain-ends tends to make the fibre substance considerably less accessible, with the result that an appreciable decrease in the fraction of accessible hydroxyl groups responsible for combination with the dye molecules takes place. This is reflected in the rapid drop in

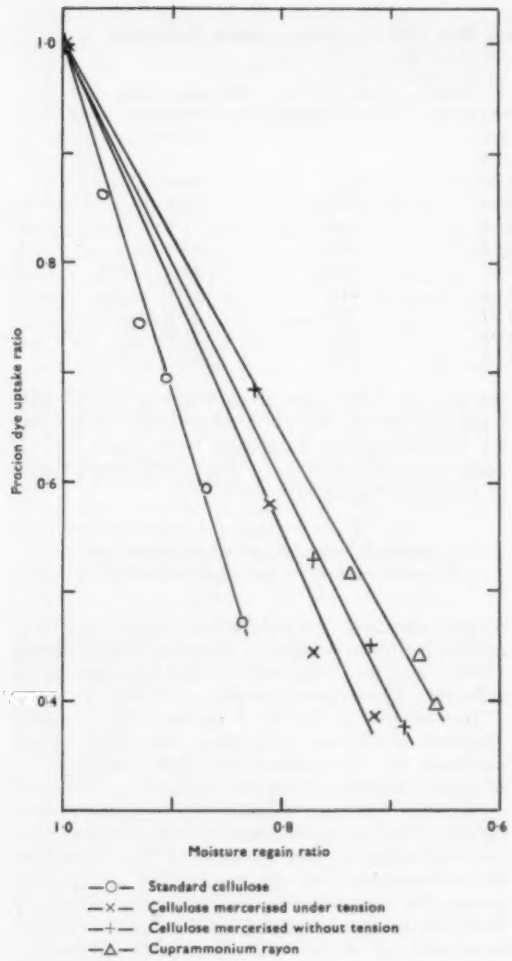

FIG. 1— Relation between Moisture Regain Ratio and Procion Dye Uptake Ratio for Hydrocelluloses prepared from Different Cellulosic Fibres

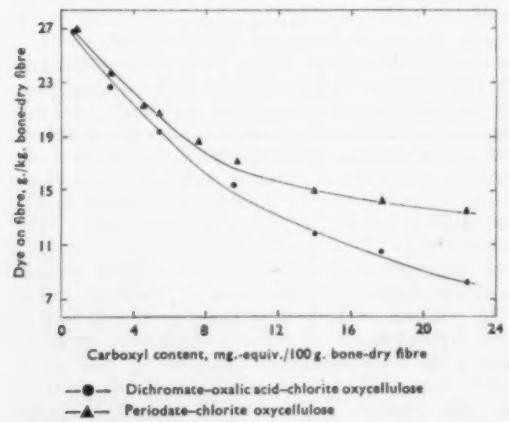

FIG. 2— Equilibrium Uptake of Procion Brilliant Red 2BS by Different Oxycelluloses

the dye uptake during the initial stages of acid action.

In the second phase the acid action is mainly confined to less readily accessible mesomorphous regions [6], which are dissolved off rather slowly, with the result that the reduction in accessible hydroxyl groups and the consequent reduction in the dye uptake are much lower. In the final stage of mild hydrolysis, the acid is unable to penetrate the inaccessible crystalline regions, and under the conditions of acid concentration and temperature used in the present work an equilibrium is established between the hydrogen ion concentration inside and outside the fibre substance. This leads to very little change in the accessible hydroxyl groups, and therefore the dye uptake tends to remain the same. With different cellulosic fibres studied, the extent of reduction in the Procion dye uptake at each of the successive stages of hydrolysis is different, and is mainly governed by two factors, viz. rate of loss in weight of fibre substance and rate of increase in fibre crystallinity during hydrolysis. Results of the present work do not support the hypothesis that, because of their much greater chemical activity, Procion dye molecules are capable of breaking fibre–fibre bonds in the crystalline regions and of penetrating the crystallites [7]. On the contrary, the Procion dye is found to behave in the same manner as direct and vat dyes, and with an increase in fibre crystallinity the Procion dye uptake decreases correspondingly.

Plots correlating moisture regain ratios with Procion dye uptake ratios for different fibres studied are linear (Fig. 1), indicating their interdependence. However, the slopes of these plots are different and always greater than unity, which shows that, with each fibre, for a specific reduction in moisture regain the corresponding reduction in Procion dye uptake is much greater. Although adsorption of water molecules (at 65% R.H.) and of Procion dye molecules is likely to take place on the accessible hydroxyl groups in the non-crystalline regions, the water molecules, being comparatively small, are likely to occupy most of the accessible hydroxyl groups, whilst the Procion dye molecules by virtue of their larger molecular size are not capable of having complete access to all the hydroxyl groups responsible for moisture regain. The reduction in adsorption of direct dyes such as Chrysophenine G (C.I. Direct Yellow 12) or Chlorazol Sky Blue FF (C.I. Direct Blue 1) is considerably less than that of Procion Brilliant Red 2BS at each successive stage of hydrolysis, which indicates that the adsorption of direct dyes does not occur entirely at the accessible hydroxyl groups, but certain other adsorbing surfaces also play an important part [8].

When standard cellulose is treated with specific oxidising agents so as to convert the accessible alcoholic groups into carboxyl groups, a gradual decrease in Procion dye uptake is observed (Fig. 2). The reduction in dye uptake is more marked with dichromate–oxalic acid–chlorite oxycelluloses, where primary alcoholic groups are converted to carboxyls [9], than with periodate–chlorite oxycelluloses,

where the oxidising action is mainly confined to secondary alcoholic groups [19].

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Dyeing Properties of Mature and Immature Cotton

NILS-BERTIL FURVIK

Laboratory dyeing experiments, carried out with direct dyes on immature and mature cotton fibres of known origin, showed that the maturity did not affect the amount of dye absorbed at equilibrium. The absorption and desorption rates, however, were higher for immature than for mature fibres. Mercerisation of the fibres before dyeing did not greatly affect the differences.

The causes of why immature fibres in general and especially in neps look lighter in colour than the rest of the fabric are discussed. A theory is put forward that, besides the effect of optical differences, the differences in depth are caused by the more rapid desorption of dye from immature fibres. Such differences would be exaggerated by unsuitable processing conditions, e.g. during rinsing, which was confirmed by some laboratory dyeings on fabric samples.

From the results, it was predicted that, in order to obtain an even colour on a fabric containing immature as well as mature fibres, dyeing should not be carried on until equilibrium is reached and that rinsing and aftertreatments should be carried out so that the dye desorption will be as small as possible.

INTRODUCTION

It is well known that the degree of maturity of a cotton fibre has a great influence upon many of its properties, both physical and chemical. As early as the nineteenth century, it was observed that thin-walled or immature cotton fibres dye differently from normal ones. This often makes it a hard and sometimes an impossible task to dye a piece of cotton fabric an even colour if it holds a fairly large proportion of immature fibres. The greatest difficulties are encountered with a fabric containing neps. That neps consist mainly of immature fibres was shown in 1923 by Clegg and Harland [1] and confirmed in recent studies, e.g. by De Meulemeester, Raes, and Backer [2].

Although the abnormal dyeing properties of neps and immature cotton fibres have been known for quite a long time, very little information has been published on the subject. The dyemakers, however, often state which dyes are unsuitable, and which suitable, for use in dyeing a "neppy" fabric.

In 1927 L. G. Lawrie [3] stated that certain dyes will dye neps to almost the same colour as the rest of the fabric, while other dyes will give the neps a lighter colour. If the fabric is mercerised before it is dyed, the colour differences between the neps and the rest of the fabric will generally decrease. A calendering treatment will often make the differences more marked, however. Rose [4] also mentioned the dyeing differences between mature and immature fibres, which he considered to be caused by differences in fine structure.

In 1947 Goldthwait *et al.*[5] described a dyeing test for determining the maturity of a cotton. In this method the cotton is dyed for 45 min. in a boiling dyebath containing a mixture of a green dye, Chlorantine Fast Green BLL (Ciba), and a red dye, Diphenyl Fast Red 5BL Supra I (Gy). The fibres are then rinsed in cold water, placed in boiling water for 30 sec., rinsed in cold water, and dried. After this treatment, the mature fibres are dyed red, and the extremely immature fibres green.

The method has been specified in detail by ASTM Committee D-13 on Textile Materials[6], which describes it as a *Proposed Method of Test for predicting Differential Dyeing Behaviour of Cotton.* The committee states that generally the results are well correlated with the maturity of a cotton, but they may be influenced also by other factors, e.g. the fineness, natural colour, and storage damage of the cotton.

Armfield and Boulton [7] have used Goldthwait's method on rayons of different fineness, and consider that the differences in colour are due to the great difference in half-dyeing times of the two dyes and to the differences in surface area between different fibres.

Recently, Rony [8] has discussed the differential dyeing method.

SCOPE

The differences in colour between immature and mature fibres may be due to several causes. One reason may be a difference in dye content caused by— (*a*) differences in amount of dye absorbed at equilibrium, (*b*) differences in rates of dyeing, (*c*) differences in rates of desorption during rinsing and scouring after dyeing.

Rate of dyeing will, of course, affect the dye content of the fibres only if the dyeing is interrupted before equilibrium has been reached. This is generally the case in industrial dyeing. Boulton *et al.*[9] have, for instance, found that rayons having practically the same amount of dye absorbed at equilibrium greatly differed in rates of dyeing owing to different finenesses and differences in fine structure.

Differences in colour may be caused also by optical effects, as it has been observed that, of two fibres of the same composition but of different diameters, the fibre of lower diameter will appear lighter in colour, even though the dye concentration is the same in both fibres. (An immature or thin-walled fibre will act as the fibre of lower diameter in this respect.) This phenomenon has been widely reported in the literature, for rayon fibres [7, 10] and for cotton [11].

In order to find which of the causes mentioned above are responsible for the differences in colour between dyed immature and mature cottons, rates of absorption and desorption together with the amount of dye absorbed at equilibrium have been measured when unmercerised and mercerised cottons of different maturity are dyed with certain direct dyes.

EXPERIMENTAL

Cotton

In order to eliminate genetical and environmental variations as far as possible, some of the experiments have been carried out on fibre samples of different maturity from the same cotton plants. The samples were taken from bolls picked 25, 42, and 57 days respectively after flowering. The 57-day cotton came from normally developed, naturally opened bolls. The samples were designated D&P 25, D&P 42, and D&P 57 (D&P = Delta Pine). As only small quantities of this cotton were available, some experiments have been carried out on two other cottons of very different maturity. These came from the same district in Texas, but one was a Macha Stormproof cotton and the other a Stormmaster cotton. Their maturity was determined by the A.S.T.M. sodium hydroxide swelling method [12], which for Macha Stormproof gave 88% mature fibres and for Stormmaster 41% (extremely immature). The Micronaire value of each cotton was also determined using both the normal curvilinear scale and a linear scale (the Causticaire scale). On each sample three tests were carried out. The results are given in Table I.

TABLE I

Micronaire Values

Cotton	Curvilinear Scale Mean	Curvilinear Scale Range	Linear Scale Mean	Linear Scale Range
D&P 57	3·69	0·19	54·8	2·5
D&P 42	3·34	0·12	50·0	2·0
D&P 25	2·56	0·03	34·0	0·5
Stormmaster	2·44	0·03	29·2	0·5
Macha Stormproof	4·94	0·10	68·6	1·5

Before being dyed, the cottons were scoured at the boil in sodium hydroxide (10 g./litre) under reflux for 4 hr. After 2 hr. most of the sodium hydroxide solution was drained off and fresh solution added. The cottons were rinsed with cold distilled water, then in dilute acetic acid (1 ml. per litre), and finally with distilled water until the water showed a neutral reaction. The cottons were then dried in air at 40–50°C.

As only small amounts of the D&P cottons were available, the possibility of using the same fibres after removing the dye by extraction with aqueous pyridine (40–50% pyridine by volume) was investigated. No changes in the dyeing properties of the fibres were observed, and therefore experiments were carried out on the extracted cotton.

In some of the experiments loose cotton fibres were mercerised in sodium hydroxide solution (180 g./litre) at 15°C. during 10 min., rinsed, and dried as described above before they were dyed.

Dyes

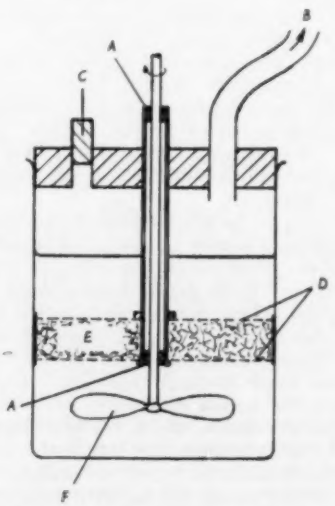
The following commercial direct dyes were used—

(1) Diphenyl Fast Red 5 BL Supra I	C.I. Direct Red 81
(2) Chlorantine Fast Green BLL	C.I. Direct Green 26
(3) Durazol Blue G 200	C.I. Direct Blue 78
(4) Chlorazol Blue G 150	C.I. Direct Blue 10
(5) Coprantine Brown RL	C.I. Direct Brown 162
(6) Coprantine Brown GRLL conc.	C.I. Direct Brown 161

Dyes (4) and (6) do not cover neps well, but (3) and (5) are excellent in this respect according to the dye manufacturers.

Dyeing Conditions

The absorption and desorption experiments were carried out in the apparatus shown in Fig. 1. In the absorption experiments 1·50 g. of cotton, conditioned at 65% R.H. and 20°C., was weighed out and distributed uniformly in the steel wire basket, which was then placed in a bath of distilled water heated to the dyeing temperature. The basket with the fibres was then weighed (so that the liquor ratio could be accurately adjusted), and placed in the preheated dyebath; the stirrer was started immediately. The liquor ratio was 250 : 1. (This somewhat elaborate procedure was worked out in order to get enough penetration and to obtain temperature equilibrium in a minimum of time; in



A Teflon bearing
B To condenser
C Sampling hole
D Wire net
E Fibres
F Stirrer

FIG. 1— Dyeing Apparatus

fact, the penetration was so good that the fibres were dyed almost as rapidly as fibres cut in a Wiley mill and distributed in a well stirred dyebath.) During the dyeing, portions were removed at intervals from the dyebath for colorimetric determinations of dye concentrations. The dyeings were normally carried on until equilibrium was attained. At this point, the fibres were rinsed on a glass filter with ice-water until the rinsing water was completely colourless and then pressed between blotting paper to remove most of the water. Finally the fibres were dried at 40–50°C.

In the desorption experiments 1·00 g. of fibres dyed to equilibrium were put in the wire-net basket, which was placed in a bath of distilled water, and the stirrer was started immediately. The liquor ratio was 375 : 1. During the desorption the bath concentration was determined colorimetrically. The desorption experiments were not carried on to equilibrium.

The amount of dye taken up by the fibres was calculated from the measurements on the dyebath samples. In some cases the calculated dye content was checked by stripping the dye from the fibres with aqueous pyridine and then determining the dye colorimetrically. The results were in good agreement.

RESULTS

From the results, a diffusion coefficient D, or rather the quantity D/r^2 (r = radius of a cylindrical fibre having a cross-sectional area equal to the average cross-section of the dyed fibres), and the affinity R were calculated by the method described by Olofsson [13].

The values reported as D/r^2 are time averages obtained from the equation—

$$\frac{D}{r^2} = \frac{(R+1)\Sigma\beta t}{\Sigma t}$$

in which β is the apparent diffusion coefficient and t is the dyeing time. The amount of dye taken up at equilibrium M_∞ (mg. per gram of fibre) was also calculated.

Equilibrium data are set out in Tables II–VII, and some absorption and desorption curves are shown in Fig. 2–4.

TABLE II

Absorption of Durazol Blue G 200

(0·08 g. Durazol Blue G 200 + 10 g. $NaSO_4$ per litre A 1 and A 2 at 90°C.; A 3 at 75°C. A 1 and A 2 unmercerised; A 3 mercerised)

Dyeing	Cotton	D/r^2	R	M_∞
A 1.1	D&P 57	5·0	310	10·3
A 1.2	D&P 57	3·3	350	10·5
A 1.3	D&P 42	5·0	360	10·6
A 1.4	D&P 25	11·6	370	10·6
A 2.1	Macha	2·0	345	10·0
A 2.2	Stormmaster	15·0	375	11·0
A 3.1	D&P 57	10·7	3500	16·9
A 3.2	D&P 42	11·8	4000	17·2
A 3.3	D&P 25	18·6	3000	16·5

TABLE III

Absorption of Chlorazol Blue G 150

(0·05 g. Chlorazol Blue G 150 + 20 g. Na_2SO_4 per litre B 1 and B 2 at 90°C.; B 3 and B 4 at 75°C. B 1, B 2, B 3 unmercerised; B 4 mercerised)

Dyeing	Cotton	D/r^2	R	M_∞
B 1.1	D&P 57	16·8	310	6·3
B 1.2	D&P 42	25·1	330	6·5
B 1.3	D&P 25	37·9	345	6·5
B 2.1	Macha	10·9	320	6·3
B 2.2	Stormmaster	49·4	375	6·6
B 3.1	D&P 57	5·5	545	7·2
B 3.2	D&P 42	5·3	580	7·4
B 3.3	D&P 25	14·3	525	7·3
B 4.1	D&P 57	42·8	1160	9·1
B 4.2	D&P 42	46·8	1020	8·9
B 4.3	D&P 25	54·8	1045	9·0

TABLE IV

Absorption of Chlorantine Fast Green BLL

(0·08 g. Chlorantine Fast Green BLL + 10 g. Na_2SO_4 per litre. Unmercerised fibres at 90°C.)

Dyeing	Cotton	D/r^2	R	M_∞
C 1.1	D&P 57	1·5	890	14·2
C 1.2	D&P 57	1·0	860	14·0
C 1.3	D&P 42	1·0	910	13·9
C 1.4	D&P 25	3·3	860	14·1
C 2.1	Macha	0·56	870	13·8
C 2.2	Stormmaster	4·7	860	14·5

TABLE V

Absorption of Diphenyl Fast Red 5BL Supra I

(0·08 g. Diphenyl Fast Red 5BL Supra I + 20 g. Na_2SO_4 per litre. D 1 and D 2 at 90°C.; D 3 at 75°C. Unmercerised)

Dyeing	Cotton	D/r^2	R	M_∞
D 1.1	D&P 57	21·8	180	7·1
D 1.2	D&P 57	20·8	190	7·2
D 1.3	D&P 42	26·9	180	6·9
D 1.4	D&P 42	23·5	165	6·5
D 1.5	D&P 25	47·8	205	7·4
D 2.1	Macha	13·2	165	6·6
D 2.2	Stormmaster	42·6	185	6·9
D 3.1	D&P 57	11·2	305	9·2
D 3.2	D&P 42	18·4	315	9·5
D 3.3	D&P 25	31·1	320	9·6

TABLE VI

Absorption of Coprantine Brown GRLL

(0·1 g. Coprantine Brown GRLL + 4 g. Na_2SO_4 per litre 90°c. E 1 unmercerised; E 2 mercerised)

Dyeing	Cotton	D/r^2	R	M_∞
E 1.1	Macha	0·24	230	9·5
E 1.2	Macha	0·16	225	9·5
E 1.3	Stormmaster	0·23	300	11·4
E 2.1	Macha	0·30	580	14·5
E 2.2	Stormmaster	0·32	830	16·2

TABLE VII

Absorption of Coprantine Brown RL

(0·1 g. Coprantine Brown RL + 4 g. Na_2SO_4 per litre 90°c. F 1 unmercerised; F 2 mercerised)

Dyeing	Cotton	D/r^2	R	M_∞
F 1.1	Macha	0·9	290	11·5
F 1.2	Macha	1·1	295	11·7
F 1.3	Stormmaster	1·5	350	12·6
F 2.1	Macha	2·2	920	17·2
F 2.2	Macha	2·3	1190	18·0
F 2.3	Stormmaster	2·9	1400	18·6

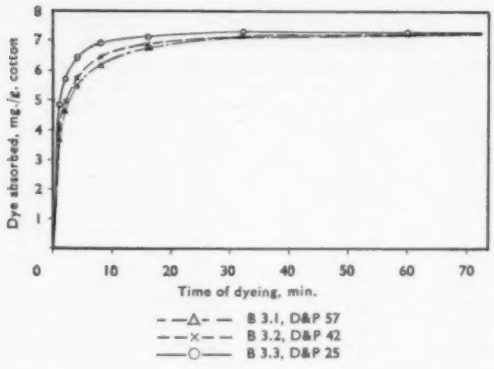


FIG. 2

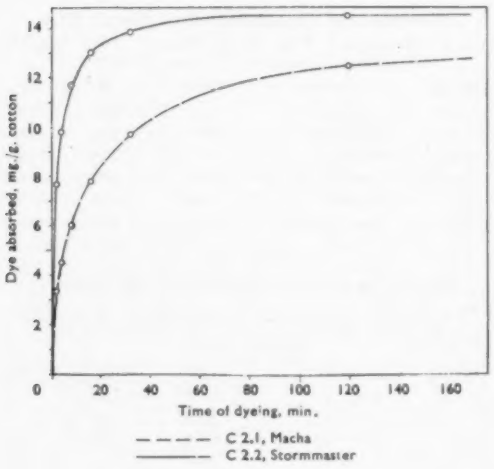


FIG. 3

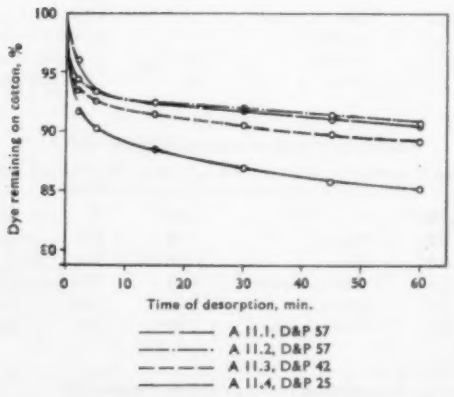


FIG. 4

DISCUSSION

The absorption experiments with D&P cotton show that mature and immature cotton absorb the same amount of dye at equilibrium (the same affinity), but that the immature fibres are dyed more rapidly. The latter can also be seen from the experiments with Macha Stormproof and Stormmaster. The desorption curves also show that the dyes are desorbed more rapidly from the immature cotton. One reason for the more rapid absorption and desorption is the larger surface area per unit weight. In Micronaire testing the air velocity is inversely proportional to the square of the fibre surface area, which means that the surface areas of D&P 57, D&P 42, and D&P 25 stand in the ratio 1·35 : 1·41 : 1·70 (calculated from the results obtained with the linear Causticaire scale). These differences in surface area, however, are not large enough to explain the differences in D/r^2, and it is therefore concluded that there are also differences in fine structure between the cottons of different maturity.

In most commercially dyed cotton fabrics the neps due to immature fibres show as light specks. Very rarely, however, though more frequently in mercerised fabrics, they show as dark specks. These differences in colour are due to either (*a*) purely optical effects or (*b*) a combination of differences in dye concentration and optical effects.

The intensity of the colour of a uniformly dyed fibre depends not only on the dye concentration and the colour characteristics of the dye molecules but also on the average length of path of the light in the dyed fibre wall. As the immature fibres have a thinner wall than the mature ones, the former will appear paler if the dye concentration is the same in both kinds. This phenomenon has been observed also in these experiments both visually and by measurement of reflectance with a Beckman spectrophotometer. However, the differences that were observed did not seem to be as large as those that often are seen between the neps and the rest of the fabric in commercially dyed fabrics. This observation suggests that there is often a lower dye concentration in the immature fibres in the neps than in the fibres in the rest of the fabric.

A commercial dyeing is generally not carried on to equilibrium, and according to the results of the absorption experiments the immature fibres should then have a higher dye concentration than the mature fibres. The higher concentration will counteract the optical effect, and under certain conditions the difference in concentration will be sufficiently large to make the neps appear darker than the rest of the fabric, especially if the fibres are ring-dyed.

Theoretically, the lower concentration of dye in the immature fibres will then be due either to more rapid desorption of dye from these fibres during rinsing and other wet aftertreatments or to the immature fibre assemblies like neps being harder for the dyebath to penetrate. The latter is probably not the case, while the desorption experiments have demonstrated that the dye is in fact more rapidly desorbed from immature fibres.

In order to check this theory, a few laboratory dyeings were carried out on a scoured, bleached fabric having a medium nep content. Fabric samples were dyed in dyebaths with poor or very good agitation (ultrasonic vibration) to about the same depth. Dyeing times were 45 and 60 min.,

and the temperature was 75°C. The dyes used were Durazol Blue G 200 and Chlorazol Blue G 150.

The neps did not show up much as light specks on any of the dyed samples, provided that these were rapidly rinsed in cold running water. The conclusion was that the neps were penetrated so easily that poor penetration cannot in general be the reason for the neps being lighter in colour: indeed, the neps on the samples seemed rather to be better penetrated than the rest of the fabric. On the other hand, if the rinsing was done with warmer water (around 40°C.) for 10 min., the neps showed very clearly as light spots.

From these and the earlier experiments it is concluded that the immature fibres in the neps appear considerably lighter in colour than the rest of the fabric in many commercially dyed fabrics as a result of a combination of the optical effect mentioned above and a lower dye concentration. The latter is caused by desorption of dye during rinsing and other wet aftertreatments, and will be greater if these operations are carried out under such conditions as high temperatures and long times.

In order to avoid the immature fibres appearing lighter on a fabric containing both immature and mature fibres, the dyeing should not be allowed to approach too near equilibrium, and rinsing and aftertreatments should be done so that dye desorption will be as small as possible. In such a case the immature fibres will hold more dye than the mature ones, which is necessary to obtain a uniform colour, owing to the optical effect mentioned earlier.

On the other hand, if the neps are dyed darker, a longer dyeing time will probably even out the differences.

The experimental results from the dyeings on mercerised cotton fibres indicate that the maturity affects the dyeing properties in the same way as for unmercerised fibres. This is somewhat surprising, as the common opinion is that a mercerisation treatment of a neppy fabric will improve the evenness of colour after dyeing. This lack of agreement may be due, however, to the fact that, when a fabric is mercerised industrially, the fibres in the yarns are normally under tension and therefore will swell less than the loosely bound fibres in a nep.

* * *

I wish to thank Dr. John T. Pressley, Field Crops Branch, U.S. Department of Agriculture, and Dr. Leonard Smith, National Cotton Council of America, who were kind enough to supply me with the cotton. I am also very grateful to Professor N. Gralén and Dr. J. Lindberg for their interest in this work and to several others at the Institute for occasional assistance.

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The Editor does not hold himself responsible for opinions expressed by correspondents

Quantitative Analysis of Wool–Terylene Blends

Quantitative analyses of wool–Terylene blends may be carried out by destroying either the wool with sodium hypochlorite or the Terylene with hydrazine. Another practical method is based upon the difference in densities, but this requires considerable experimental skill. One of the most marked differences between wool and Terylene lies in their regains, and this property has now been used to determine the composition of a number of blends.

If W is the regain of wool, T the regain of Terylene, and R the regain of the unknown sample, all measured under identical conditions, then the weight-fraction x of wool in the mixture can be calculated from the relation—

$$R = xW + (1 - x)T$$

The method used was as follows. Duplicate samples (about 4 g. each) of wool, Terylene, and the unknown fabric were treated with alcohol and with ether in a Soxhlet extractor. After the clean samples had been oven-dried at 110°C. for 4 hr. they were allowed to cool in a desiccator over phosphorus pentoxide before being weighed. The samples were then transferred to another desiccator containing aqueous sulphuric acid (R.H. 87% at 20°C.), allowed to come to equilibrium during 2 days, and weighed again.

Reproducibility of the observations was good; the standard deviation for 16 observations comprising duplicate measurements on 8 samples cut from the same roll was $\pm 0{\cdot}5\%$.

The absolute accuracy of the values is less certain. It is known that minor variations in the regain of wool can be attributed to the presence of dyes [1] and to differences in quality [2]. The presence of titanium dioxide in the Terylene may also cause a slight deviation from the absolute value. Undoubtedly, the main systematic error in the simple

determination described above is due to the fact that the regains are calculated on the oven-dry weights, and are not strictly accurate. Wool dried in an oven at 110°c. can still contain 0·6% moisture[3]. However, the same systematic error is included in the wool and Terylene standards as well as in the unknown, and as they *almost* cancel in the calculation, the percentage of wool in the blend is usually low by about 0·5%. If great precision is required, then the true regain must be determined. If the water-absorption characteristics of the wool and Terylene standards do not match those of the components of the unknown mixture, the systematic error will be larger. Analysis of a known blend of wool–Terylene by chemical methods gave the following values for the wool content: 55·7 ± 0·6% using *o*-chlorophenol and 55·4 ± 0·5% using hydrazine (J. C. Atkinson, personal communication). The regain method gave 54·7 ± 0·5%.

The main disadvantage of the method is that it requires a long time to complete the determination. On the other hand, the actual operating time is probably less than in any other method. Another advantage is that the sample is not destroyed, so the result can be checked at any time. By using wool and Terylene standards the more difficult task of controlling and measuring the temperature and the relative humidity is eliminated.

Analysis of binary blends by regain is not confined to wool–Terylene. The principle can be applied to any mixture provided that the regains are sufficiently different: the greater the difference in regains the greater is the precision of the analysis, and the conditions of relative humidity should be adjusted accordingly. If the difference exceeds 10%, as it can with blends of wool (or viscose rayon) with nylon, Terylene, polyvinyl chloride, or polyvinyl cyanide fibres, the accuracy of the analysis should be better than 0·7%. A useful degree of accuracy, ± 3%, is still possible even if the difference in regains is as small as 3%. In favourable circumstances ternary blends may also be analysed by measuring the regains at two different relative humidities.

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18th February 1958

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Notes

Meetings of Council and Committees
March

Council— 5th

Finance and General Purposes— 12th

Publications— 18th

Colour Index Editorial Panel— 3rd and 19th

International Federation 1959 Congress Planning and Co-ordinating Committee— 5th.

Deaths

We regret to report the loss by death of Mr. G. T. Halliwell, Mr. H. C. Olpin, and Mr. T. M. Young.

Coat of Arms

Readers may be interested in the symbolism of the Society's Coat of Arms, illustrated in the frontispiece to the July 1957 issue of the *Journal*. The shield, which is the main part of the Coat of Arms, incorporates several elements used in the design of the Presidential Badge of the Society presented in 1951 by the Worshipful Company of Dyers of the City of London. The shield is divided into three areas of heraldic colour, with purpure and or in the upper areas and azure in the lower. These approximate to the subtractive primary colours. In the lower area is a silver hexagonal benzene ring, symbolising the chemical and technical achievements of the industry, placed between two slips of the grain-tree. In the upper areas are placed emblems representing the madder and indigo plants respectively.

The dexter supporter is the goddess Iris, who, as a messenger of the gods, had the rainbow as one of her symbols. She was, in fact, accepted as the goddess of the rainbow, which, in this case, is symbolic of colour in general. As a messenger of the gods she carries in her right hand a caduceus or herald's staff.

The sinister supporter is a dyer in seventeenth-century attire holding a skein of silk.

The crest is a purple iris flowering on a wreath of gold and purple, the allusion being to the dexter supporter already described.

The Latin motto *Scientia Coloris Ministra* ("Science is the Servant of Colour") refers in general terms to the aims both of the Society and of the industry as a whole.

Election of Fellows

At the meeting of Council held on 5th February 1958 the following were elected Fellows of the Society—

Ralph James Mann
(*Spondon, Derby; Superintendent, Dyeing and Finishing Development Department, British Celanese Ltd.*)

Wilfred Mather
(*Ireland; Consulting Technologist to Leather Manufacturers*)

Reginald Williamson
(*Castleford, Yorkshire; in charge of Technical Service for Textile Auxiliaries and Fluorescent Brightening Agents, Hickson & Welch Ltd.*)

John Barritt, B.Sc., A.R.C.S., A.R.I.C., F.S.D.C. Gold Medal of the Society

At the meeting of Council held on 5th February 1958 it was resolved, on the recommendation of the Society's Medals Committee, that the Society's Gold Medal be awarded to Mr. John Barritt "for exceptional services to the Society as Chairman of the *Colour Index* Panel".

Keith McLaren, B.Sc., F.R.I.C., F.S.D.C. The Worshipful Company of Dyers Research Medal 1956–1957

On the recommendation of the Council of the Society, the Worshipful Company of Dyers has awarded its Research Medal for 1956–1957 to Mr. K. McLaren, for a series of papers on light-fastness testing and fading of dyes.

Fred Atack Silver Medal of the Society

At the meeting of Council held on 5th February 1958 it was resolved, on the recommendation of the Society's Medals Committee, that the Society's Silver Medal be awarded to Mr. Fred Atack "for services to the Society as Honorary Secretary of the Scottish Section 1947–1957".

Fastness Tests Report

Reprints of the First Supplement to the Third Report of the Fastness Tests Co-ordinating Committee, published in the January 1958 issue of the Journal, can now be purchased from the Society. This publication details the changes and additions agreed at the meeting of the ISO Colour Fastness Sub-committee held in New York in September 1956, and thus brings the Third Report up to date. It is therefore advisable that all those who are using the *Standard Methods for the Assessment of the Colour Fastness of Textiles* should obtain a copy of the First Supplement.

Preservation of Historical Dyes

At a meeting of the Historical Records Committee held on 31st January 1958 it was reported that there had been great difficulty in obtaining samples of Ionamine dyes for the Perkin Centenary exhibition held by the West Riding Section in the Bradford Institute of Technology, and it was pointed out that, with limited storage capacity in technical colleges and dyehouses, it was inevitable that older dyes would be discarded to make room for newer dyes.

In order to preserve samples of natural dyes in danger of extinction and synthetic dyes of historical interest, the Committee decided to accept such dyes for safe storage, and it now invites dye manufacturers, dyers, and educational establishments to forward samples to the Society for preservation.

It is intended to restrict the samples to those of outstanding importance and, preferably, to first samples of any particular dye. Samples should, of course, be labelled and dated.

The Perkin Centenary Celebration

The organisers of the Perkin Centenary Celebration have completed their accounts and the organisation has been wound up. The result of the appeal to date is as follows—

	£	s.	d.
Donations in cash	13,208	10	0
Donations under covenant ...	23,077	0	0
Bank interest received (less charges)	203	11	1
	36,489	1	1
Expenses incurred in administration (including administration, celebration, and exhibition at the Science Museum)	3,236	10	7
Total amount available to the Perkin Centenary Trust over the years 1955–1965	£33,252	10	6

The total available funds indicated above have now been handed over to the Perkin Centenary Trust, and the following awards have been made during 1957— one Perkin Centenary Fellowship, three Perkin Centenary Scholarships, and one Perkin Exchange Scholarship.

The list of donors includes the names of some 160 firms.

Asociacion Argentina de Quimicos Textiles y Coloristas

The A.A.Q.T.C. was formally constituted on 12th July 1957 in Buenos Aires, when Dr. Emilio Haim was elected president. The main aims of the Association will be to increase scientific and technical knowledge of textile chemistry, to promote research in this field, to cultivate professional relations between members and with similar societies both at home and abroad, and to pay special attention to technical education. The address of the A.A.Q.T.C. is Av. Belgrano 624, Buenos Aires.

Trichloroethylene in Sewage

The Annual Report for 1956 of the Scientific Adviser to the London County Council states that three examples of sewer detritus were found to contain up to 10% of trichloroethylene. The report emphasises that, on account of its narcotic and toxic properties, this solvent should never be allowed to enter a sewer: even quite small amounts can be a serious hazard to men who are cleaning the sewers.

Indian National Chemical Laboratory, Poona

Dr. K. Venkataraman, F.S.D.C., has become the first Indian Director of the National Chemical Laboratory, the post having been occupied previously by Professor J. W. McBain and Professor G. I. Finch. Dr. G. M. Nabar, also a member of the Society, has been appointed to act as Director of the Department of Chemical Technology of the University of Bombay.

The German Technische Hochschulen

In view of the current interest in technical education in this country, a brief survey by Dr. J. Horne (*Nature*, **180**, 1445–1448 (28 Dec. 1957)) of the development of the *technische Hochschulen* in Western Germany is particularly opportune. During the eighteenth century there sprang up in Germany modern secondary schools (*Realschulen*), which challenged the classical grammar schools (*Gymnasien*). Simultaneously trade or technical schools arose in many German towns, notably Berlin. Subsequently these improved their status and were called "academies". During the 1820s and 1830s many of these greatly expanded institutions became university centres of science and technology, the *technische Hochschulen* of today. A powerful stimulus for this development came from the Polytechnics of Prague (1806) and Vienna (1815), themselves created by the Austrians on the model of the famous École Polytechnique of Paris.

An outstanding feature of the *technische Hochschulen*, in addition to their high standards of instruction and research, is the Studium Generale: a choice of lecture courses or individual lectures and discussion groups on a wide range of subjects is offered annually by the faculties of humanities or general subjects.

OBITUARY NOTICE

Edgar Allan Swift

Mr. E. A. Swift, who died on 1st June 1957, had a life-long association with the dye industry. He was born at Loughborough in 1881 and after school became apprenticed to the dyeing trade in Nottingham. After being agent for George Kenyon in Manchester, who represented Karl Oehler, Offenbach, from 1907 to 1911, he became agent for Sandoz Chemical Works of Basle, and when the associated British concern, Sandoz Chemical Co. Ltd., was formed in 1911 he was appointed Managing Director. In the nineteen years he held that position the company's business greatly expanded in dyes, chemical auxiliaries, and other fields.

Mr. Swift attended Leeds University part time during the three sessions 1908–1911, undertaking special work on the detection of dyes on the fibre, and he retained throughout his life a special affection for the Department of Colour Chemistry and Dyeing.

During the 1914–1918 war Mr. Swift carried out a number of missions for the Board of Trade, and played a considerable part in obtaining raw materials for Britain and the practical knowledge needed for the production of speciality dyes.

Mr. Swift left the Sandoz Chemical Co. in 1931, and in that year and early 1932 visited North and South America to enquire into the possibility of exports of British dyes and chemicals. On the voyage he had the experience of being shipwrecked on an island off the coast of Chile. Mr. Swift gave some interesting lectures about his journey, and was able to supply the Board of Trade with some useful information.

In 1935 he founded Allied Colloids (Bradford) Ltd., of which he was Chairman till the end of his life. The French dye manufacturers united under Établissements Kuhlmann asked Mr. Swift some years before the 1939 war to undertake their representation in Great Britain, and this has been held in unbroken sequence by the Company ever since. The products of the French concern, now the Compagnie Française des Matières Colorantes, thus became known throughout the dyeing trade in this country. With the over-running of France by the German army in 1940 the British Government seized French ships carrying dyes and auxiliaries, and Mr. Swift obtained the concession to market these products with a view to securing their full market value. The proceeds of these sales were repatriated to France at the end of the war. In 1947 Allied Colloids began a happy and steadily developing association with the Badische Anilin- und Soda-Fabrik AG., of Ludwigshafen a. Rhein, Germany.

Mr. Swift was a militant member of the Society of Dyers and Colourists, which he joined in 1904. He worked untiringly for the Society to obtain a charter. He was Chairman of the West Riding Section for two years and was an esteemed member of the Council of the Society. He also served on the Council of the Textile Institute under the Presidency of the late Mr. John Emsley.

It is widely acknowledged that Mr. Swift showed forthrightness in encouraging younger people to go ahead on the practical and academic sides of the chemical and textile industries and readily gave them advice and help.

One of his great interests outside business was horsemanship: he was a member of the Bramham Moor Hunt for many years, and it was not until 1949 that he put away his polo sticks after playing for a long period with the Toulston Polo Club at Tadcaster; he was also a founder member and a past-president of the Ilkley Pony Club. He was a past-president of the Bradford Rugby Union Football Club and a supporter of many other sports organisations.

New Books and Publications

Précis des Matières Colorantes Synthétiques Tome II— Matières colorantes

By Henri Wahl. Pp. 399. Paris: Presses Universitaires de France. 1957. Price, 2800 francs.

With two exceptions, both encyclopaedic, few books on the constitution and the synthesis of dyes have appeared in recent years. This handy volume, the second of a projected series of three and the first to appear, deals solely with the dyes themselves, leaving the discussion of the intermediates and of the processes of dyeing and printing and the fastness properties of dyes to the first and third volumes respectively. Professor Wahl's opportunity was great, but in some respects he has not taken full advantage of this chance to touch upon the more recent developments.

The first quarter of the book constitutes an introduction to the subject. In it, the origin of colour and the definition of its terms, as well as old and present-day theories of colour and constitution, are followed by a fairly comprehensive explanation of the terminology and nomenclature of dyes. Their classification according to both constitution and method of application is also considered fairly and carefully. Theories of colour and constitution, rarely capable of covering all coloured compounds, are given on a historical basis, but it is felt that a more critical approach to this topic might have been beneficial. This section also includes an interesting discussion of the economic factors affecting the dye industry, and production figures for various countries are given for specific dyes. The fastness properties of dyes are briefly mentioned, but the space given to this topic is not commensurate with its importance and could have been increased or, more appropriately, the subject could have been left for the third volume.

The remainder of the book is concerned with the preparation, properties, and structure of dyes and is divided according to their chemical constitution. It is clear from these chapters that Professor Wahl's knowledge of his subject is profound, and that he is able to present it lucidly and attractively. This is especially helpful for students who are commencing their studies of dye chemistry. His introduction to most classes of dyes is on a historical basis, and credit is given to the chemist concerned, but the literature references are rare and are confined to the more recent developments in the sphere of colour and constitution and in the phthalocyanine field. The text is liberally interspersed with chemical formulae, which, in nearly all instances, are self-explanatory.

Azo dyes, as befits their numerical superiority, are (with the exception of the metallisable dyes of this class) discussed thoroughly, and the structural factors affecting the substantivity of the direct dyes are dealt with in a comprehensive manner. Similarly, the subject of the insoluble azoics is covered in detail, and the rather cramped formulae at one stage can detract little from the value of this section. The historical background and many formulae are given in the chapters which cover the dyes of the triphenylmethane, phthalein, xanthen, and acridine classes, although, here again, some references to the original literature would be useful.

In dealing with the sulphur dyes, emphasis is laid upon their origin and historical background, and constitutions are discussed from both degradative and synthetic aspects. In the same way, a very comprehensive discussion of the preparation, structure, and use of dyes of both the phthalocyanine and the indigoid classes is presented. In the last main section, the important dyes based on the anthraquinone molecule are dealt with in great detail. In this, as in some earlier chapters, schematic drawings of the manufacturing plant for certain dyes are given, but, since the accompanying description of the operation is very brief, their value is not as great as might have been expected.

An index of the dyes of all classes is given and, although occasional difficulties are met with, is quite helpful. All in all, this is a well written book covering all the main features of the chemistry of dyes and should be very useful for students, for whom, in the main, it is intended.

A. R. Thompson

Textile Chemistry and Testing in the Laboratory

By Rose W. Padgett. 1956. Pp. iv + 147. Typescript reproduction, Spirax binding. Minneapolis: Burgess Publishing Co. Price, $3.50.

This is a systematic notebook to accompany studies in the Clothing and Textiles School of Home Economics at Purdue University, Indiana. This kind of school and the courses it organises are unfamiliar to the universities of this country, and to that extent the comparison with textile chemistry textbooks of more orthodox plan is interesting. The equivalent arrangement of studies would, in this country, probably be undertaken in a college of domestic science, and it is in this field that the book is likely to have its greatest direct value.

In textile chemistry schools the treatment would be regarded as wide and superficial, and there is, in this country, a prejudice against the laboratory companion which includes blank spaces for the student to put in his own sketches and questionnaires which rigidly determine the routine of analytical examination. The whole laboratory teaching appears as a drill, which, without careful accompanying supervision, may discount initiative. In fact, the author claims that if the spaces are filled in when the experiment is completed, no notebook is needed!

On the other hand, there is evidence of a very fresh and at times unconventional approach in the teaching methods, and schemes for fibre identification by both visual and chemical examination are

carefully thought out. It is evident that little in the way of chemistry is demanded, and a classification of dyes into three groups —(1) those applied directly (home dyes), (2) mordant dyes, and (3) those developed by treating with an acid— might startle many members of the Society.

Systems for examining faults developed in use, and for defining such allied properties as fastness and the identification and removal of stains, have a number of interesting features. It is difficult to see what kind of use the student is to make of his or her knowledge afterwards. There seems insufficient for an introduction to the textile industry or even, for that matter, to local dry-cleaning and dyeing businesses. The buyers of large stores would benefit, but what is really striking is the large amount of space devoted to information that suggests an extremely widespread custom of home dyeing, including such elaborations as specialised bleaching methods, stripping with all the reagents at the industrial processer's command, and professional thoroughness in the evaluation of fastness in the newly bought garment.

The bibliography is voluminous and uncritical, and must include many references well beyond the student's capacity as reflected by the text.

H. A. TURNER

Man-made Fibres

formerly Artificial Fibres

By R. W. Moncrieff. Pp. x + 661. London: National Trade Press Ltd. Price, 65s. 0d.

This new edition of the former *Artificial Fibres* has been considerably expanded to include the more recent developments in fibre manufacture.

Part I, which deals with the structure and the properties of fibres, is only slightly different from the second edition. The treatments of tenacity and molecular-weight determination have been expanded, but in the case of molecular weights the treatment remains very superficial. Some attempt has also been made to differentiate between graft, block, and copolymers, though here, again, one feels that the author's interest does not lie in the general theoretical aspects of polymer chemistry.

In Parts II and III the regenerated fibres have been thoroughly dealt with, and the author has obviously gone to considerable trouble to obtain as much information as possible on the recent cellulose triacetate fibres from the aspect of manufacturing methods and properties. Besides the new work on triacetate fibres, additions have also been made to the chapter on viscose rayon, details of the formation of chemical crimp and the effect of nuclear radiation on the fibre being given. A further chapter has been added on chemically modified cellulosic fibres (e.g. cyanoethylated cotton) and also a short account of the manufacture of Cellophane, though these are not within the scope of the title of the book.

Part IV has been greatly enlarged with the introduction of the new nylon-type fibres and also the new acrylic fibres. Recently a number of fibres of the latter type have come on to the market, and the author deserves considerable praise for the thorough way in which he has collected all the obtainable data on such new fibres, e.g. Verel, Creslan, Courtelle. A chapter on metallic yarns is also a welcome addition.

Part V, dealing with the processing of man-made fibres, includes three new chapters on control of static, textured yarns, and non-woven fabrics.

In all, the book has been thoroughly revised and brought up to date in this edition. In the main, the amount of data supplied on specific fibres is excellent, but general theoretical considerations are often ignored; thus, no mechanism, even of an elementary type, is given for addition polymerisation, and though initiators are continually mentioned by name, their mode of action and importance are completely ignored. The author has included in the book many flow-sheets describing the manufacture of fibres; these are of the type often supplied by firms to schools, and are out of place in a book for specialists, appearing rather ridiculous in such a context.

The book also includes a considerable amount of material on the use of each specific fibre. As most fibres of any one type tend to have the same major uses, this often becomes tedious and repetitive. One feels that the author has merely transcribed the circulars put out by manufacturers without using any discrimination as to the actual value of the fibre in commerce.

The book is carefully written, with few minor mistakes in the text, though quinque- and tervalent carbon atoms occur occasionally. In all, it is a thorough and gentle introduction to fibre technology, involving no arduous brain work for the reader, and giving an excellent summary of the commercial fibres and their processing.

R. S. ASQUITH

Wasserdichtmachen in Rezeptform

By Rudolf Günther. Pp. 169. Mönchen-Gladbach: Lapp-Verlag. 1957. Price, DM 5.85.

This small book is made up mainly of recipes and processing instructions for textile-waterproofing and -coating mixtures. These are divided into air-permeable and air-impermeable types and are based amost entirely on proprietary products. In addition, there are short sections on the laboratory preparation of patterns, coating machinery, tests for proof, and faults. It is clear that the author has intended to produce a practical manual on waterproofing rather than a comprehensive work, and has achieved a considerable measure of success. It is of handy pocket size and covers a large number of products. The book could have been improved by a little more expertise (although the latter is much more in evidence in the section on Macintosh fabrics) and a little less pruning of manufacturers' recommendations, where some of the omissions will lead to definitely misleading results. For example, avoidance of non-ionic scouring agents is stressed in preparing patterns, but the fact that these should be cut, not torn, is not mentioned. Again, in drying after impregnation the point is omitted that, in general, condensation proofs should not be overdried nor wax

proofs underdried. In silicone proofing no attention is drawn to the fact that the emulsifying agent must be labile.

German authors do not appear to set great store by indexes, and this book is no exception to the trend, in that its arrangement is not alphabetical and that some of the references given do not agree with the text (e.g. No. 188d and 192). There is an alphabetical list of specialities given at the end which could be used for cross-referencing, and in the next edition, which will certainly be called for in the not too distant future, one would like to see this used, with notes on the products at present included in the list but not in the body of the work.

A number of interesting photographs are included, particularly those from the Chemische Fabrik Pfersee G.m.b.H. in the faults section. In the section on testing it is clear that greater stress is placed on the Bundesmann test here than in the country of its origin: penetration figures, for example, are hardly considered. The statement that the expression of absorption figures as a ratio against those of unproofed material is the most successful means of interpreting results obtained on this apparatus will surprise many readers.

Although very many of the specialities discussed are not of active interest in Britain, at the price the book is well worth purchasing for its general usefulness to those involved in the coating or the waterproofing of textiles. No similar work appears to exist.

S. R. Cockett

Manuel d'Initiation à l'Étude de la Science des Couleurs

Pp. 59. [1956.] Price, 350 Belgian francs.

Recueil des Formules et Tables de Colorimétrie

à l'usage des laboratoires industriels

Pp. 61. 1956. Price, 250 Belgian francs.

By Frantz Braun. Brussels: ELPI (Édition–Librairie–Publicité Internationales).

There appears to be a need in French for an introduction to colour science which would steer a middle course between very detailed works and purely popular treatments. The author has therefore produced these two slim volumes for technicians in the paint, textile, and paper trades. The mathematical treatment is kept to the minimum, and each concept is clearly defined as the text proceeds, so that the result is a clearly readable exposition. In the introductory volume, definitions are dealt with at the beginning, and are followed by short chapters on the identification and the physical characteristics of colour. Mixtures and their analysis, error, spectrophotometers, and photocolorimeters are then covered in turn.

So far, the book is a simple exposition of some of Wright, Hardy, Hunter, and Judd, but original work with instruments developed at the University of Louvain is subsequently described. The photocolorimeter Lv3 refers to white automatically between the three tristimulus filters used, and, including calculations, is claimed to give within 5 min. and with very good reproducibility a result in trichromatic coefficients. From this has developed a spectrophotocolorimeter which rapidly gives a signature and meets the means of the average industrial laboratory. A glossmeter Lv20, again inexpensive, has also been developed by the University.

The Lambert–Beer law and its applications are next described, followed by a review of the practical applications of colorimetry and goniometry. This portion has obviously been written with a view to demonstrating to a larger audience the useful information which may be obtained from relatively cheap apparatus. The book bears the stamp of the professional teacher and has lost little by simplification. It should have a wide appeal. The adjective tables supply the formulae and numerical data for the application of the theory outlined in the introductory volume. As far as English readers are concerned, the elementary theory is already covered elsewhere, but colour physicists and others will no doubt be interested in the Louvain instruments and will probably find it useful to have the tables together in one volume.

S. R. Cockett

The Chemical Industry during the Nineteenth Century

A Study of the Economic Aspects of Applied Chemistry in Europe and North America

By L. F. Haber. Pp. x + 292. Oxford University Press. 1958. Price, 45s. 0d.

Because of its complex technology the nineteenth-century chemical industry has allegedly escaped the attention of economic historians. So Mr. Haber sets out to fill this gap. In one vital respect his approach differs from that of most industrial historians. Instead of tracing the growth of the industry in a single economy, he concentrates on certain basic products, describing the progress made in their production in the advanced Western economies of the nineteenth century.

First the development of the industry is traced up to 1870. The rapid growth of the British soda industry is considered in some detail, particularly in South-west Lancashire and on Tyneside. There is an interesting comparison between the diffusion of chemical knowledge in France, where the state played an active rôle, and in England, where individual initiative predominated; then Haber shows how Britain's industry surpassed that of France.

Chapters V–IX cover the second main advance. Beginning with a description of the superior chemical education available in Germany by the second quarter of the nineteenth century, Haber shows the impact of new substances, particularly synthetic dyes and the ammonia–soda process, on several economies. Despite the utilisation of by-products and the recovery of sulphur, the Leblanc process could no longer compete after 1880— as regards raw materials costs— with the new Solvay process. And despite cheaper pyrites and internal economies in the chamber process for the manufacture of sulphuric acid, the contact process made considerable progress in the 1890s. Scrutinising each country to discover the extent

to which these new methods made headway, Haber explains Germany's predominance at the close of the century. British Leblanc producers found no haven from crushing competition, and the manufacture of dyes was a "disappointing story of initial success followed by a long but inevitable decline".

The last three chapters are a potpourri of leftovers. One deals with "Big Business in the Making" and traces the evolution of two exceptionally large enterprises— the United Alkali Co. Ltd. and Erweiterte I.G. Other subjects covered include leadership patterns, patent laws, government regulations, collective action, and such employee conditions as hours, wages, and welfare.

This is a useful book in so far as it provides a straightforward, readable survey of nineteenth-century developments in the industry. On the whole, however, its shortcomings outweigh its merits. The sources used (published materials often accepted rather uncritically) and the method of presentation make the book little more than a collection of tenuously connected essays which add little to current views of the industry's development. The excursions into the general economic background are rarely convincing, and the economic aspects of the study seldom seem more than fleeting shadows cast by the technological changes which constitute the substance of the book. The book thus falls between two stools: it contributes little to industrial history, and as a collection of essays it fails to grapple with the problems which call for consideration. For instance: French and German educational developments did not immediately produce large native chemical industries. Progress was initially more rapid in Britain, where industrialisation was more advanced. It would seem, therefore, that factory owners who read Berthollet and Chaptal, and who badly wanted to introduce new methods into their businesses, were more important agents in fostering native chemical industries than the advanced educational institutions of France and Germany.

One suspects that it is not the complexities of technology so much as the problems of material and analysis that have prevented economic historians from studying this and indeed many other industries. This book contributes little to a solution of these difficulties. Nonetheless, as a pioneer effort it will doubtless fill a gap on the economic history bookshelf for a long time to come.

GORDON RIMMER

New Books received

The Chemistry of the Coordination Compounds. Edited by J. C. BAILAR Jr., and assisted by D. H. BUSCH. American Chemical Society Monograph Series No. 131. New York and London: Reinhold Publishing Corpn., and Chapman & Hall. 1956. Pp. x + 834. 148s. 0d.

Measurement of Carrotting of Hatters' Fur. B.S. 2933. London: British Standards Institution. 1958. Pp. 8. 3s. 0d.

Test for Dimensional Stability of Warp-knitted Nylon Fabrics (Boiling-water Test). B.S. 2959. London: British Standards Institution. 1958. Pp. 8. 3s. 0d.

Plastics Progress 1957. Papers and Discussions at the British Plastics Convention 1957. Edited by P. MORGAN. London and New York: Iliffe & Sons Ltd., and Philosophical Library Inc. 1958. Pp. viii + 394. 50s. 0d. (Postage 1s. 9d.).

Chemistry of Carbon Compounds. Volume **IV**— *Heterocyclic Compounds. Part A.* Edited by E. H. RODD. Amsterdam and London: Elsevier Publishing Co. and Cleaver-Hume Press Ltd. 1957. Pp. xxvi + 807. 147s. 0d.

Surface Active Agents and Detergents. Volume **II**. A. M. SCHWARTZ, J. W. PERRY, and J. BERCH. New York and London: Interscience Publishers Inc. 1958. Pp. xv + 839. $17.50.

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

British Celanese Ltd.

THE AVOIDANCE OF GAS-FADING ON "DICEL" AND "TRICEL" FABRICS: TECHNICAL BULLETINS GF1A–4A— These four bulletins are entitled, *General Considerations, Notes for Dyers and Finishers, Notes for Warehousemen and Garment Makers,* and *Testing Dyed Materials for Resistance to Gas-Fading.* They are revised second editions of the bulletins originally published in 1953. GF2A contains lists of dyes (conveniently described by C.I. numbers where given) classified as having superior fastness, moderate to good resistance and as susceptible to gas-fading, respectively. GF4A includes details of five blue standards based on C.I. Disperse Blues 3 and 27. This series gives a better gradation than the earlier one, all the standards, except 5, which is virtually immune, fading in the same direction, redder.

Ciba Ltd.

CHLORANTINE FAST DYES ON YARN AND PIECE GOODS— (Cotton, Spun and Filament Viscose)— This card contains dyeings of sixty-seven direct dyes in the Chlorantine Fast range. Each is shown dyed on mercerised cotton and spun viscose rayon cloth and also in three depths on mercerised cotton and continuous filament viscose rayon yarn. In addition the degree of reservation given by each on Courpleta, filament nylon, spun Perlon, spun Terylene, bright and delustred acetate rayon and Orlon 42 is illustrated by a dyed pattern containing each of these fibres and cotton and mercerised cotton. The accompanying text, which amounts to 88 pages, contains full information on dyeing behaviour and fastness properties including figures for dyeings aftertreated with Lyofixes 8B and EW and Coprantex B and crease-resist finished with Urcol P, Lyofix CH, Phobotex FT and Pyrovatex. Rate of dyeing curves and time-temperature-exhaustion tables are supplied for each dye.

CIBANONE MICRO DISPERSE DYES IN PIECE DYEING— This card describes thirty-two vat dyes developed expressly for pigment padding. Each is available as both powder and paste, the pigment particle size being from 0·2–1 micron. Each dye is shown dyed to four depths on cotton cloth using the pad–steam process. The range of applications of these dyes is illustrated by a further thirty-two dyeings produced with either single dyes or mixtures on such diverse materials as bleached, mercerised cotton poplin, spun viscose rayon gabardine, cotton gabardine, cotton calico, cotton velvet, cotton corduroy and cotton tarpaulin material. Information provided in the text includes the leuco potentials of individual dyes under appropriate dyebath conditions. Calculation of the requisite amounts of caustic soda and hydrosulphite required for pad–jig and pad–steam application is simplified

by the inclusion of graphs relating the quantities of these required to the amount of dye present and the liquor : material ratio or liquor pick-up used in dyeing and padding.

COMBINATION SHADES ON WOOL AND WOOL/CELLULOSIC FIBRE UNIONS— This card contains recipes for producing one hundred and twenty different colours using either Cibalan or Neolan metal-complex dyes, acid dyes or Union Fast dyes (for wool–cellulosic fibre mixtures). The dyeings shown were produced on wool fabric with Cibalan dyes, the recipes for the other types of dye being formulated to give as close a match as possible when viewed in daylight and artificial light.

Clayton Dyestuffs Co. Ltd.

CIBACET DYES FOR COURTELLE— Dyeing instructions are given for applying these disperse dyes to Courtauld's acrylic fibre together with fastness data for dyeings of 21 individual dyes.

CIBALAN DYES ON ACRILAN AND ACRILAN/WOOL UNION— The majority of the Cibalan range of neutral dyeing metal-complex dyes can be applied to Acrilan to give dyeings of good fastness to light and wet treatments. Their use is largely confined to dyeing pale colours. Selected members are of interest for solid dyeings on Acrilan/wool mixtures but here also pale colours only are possible. Dyeing is carried out in presence of sulphuric acid the amount of which may be reduced by using Cibalan Salts N or S.

CHROME DYES FOR ACRILAN AND ACRILAN/WOOL UNION— A dyeing method is given for applying chrome dyes to Acrilan and Acrilan/wool mixtures on which they are of interest for producing medium to full depth dyeings of excellent fastness to wet treatments. Fastness data for dyeings of 32 dyes are appended.

DEORLENE DYES FOR ACRILAN AND UNIONS CONTAINING ACRILAN— The modified basic dyes are of interest for producing bright, full dyeings such as are required for the knitwear and hosiery trade on this type of acrylic fibre and mixtures containing it. Fastness figures for dyeings of 5 Deorlene dyes are appended.

DIRECT AND CHLORANTINE FAST DYES ON SPUN VISCOSE RAYON PIECE GOODS— This card contains dyeings in two depths on spun viscose rayon cloth of a selection of direct and Chlorantine Fast direct dyes. Since this type of material is usually crease-resisted the dyes described in this card have been selected with this end in view, giving dyeings which are substantially unaffected in hue and/or fastness to light by this finishing process. Two sets of dyeings are provided to indicate the extent to which hue changes occur, the crease-resisted patterns having been commercially treated using the process patented by Messrs. Tootal Broadhurst Lee Co. and efficiently washed and neutralised after baking. The relevant fastness data are appended alongside each set of patterns.

MILLING DYES FOR SLUBBING AND LOOSE WOOL— This card contains dyeings in five depths on slubbing of the following dyes— 18 Benzyl dyes which, although they give dyes having a light fastness < 4–5, are of interest because of brightness, 36 Benzyl Fast and Alizarin Fast dyes giving a light fastness at least 4–5 and 29 Cibalan and Cibalan Brilliant dyes.

Farbenfabriken Bayer A.G.

PADDED DYEINGS WITH INDANTHREN DYESTUFFS— This loose-leaf card contains dyeings in five depths on cotton cloth of thirty-three Indanthren vat dyes applied by the pad–jig development method. A further eighty-two dyeings are included, produced with mixtures of dyes to give a range of colours illustrating the versatility of these dyes when applied by this method. The text includes details of the vat-acid padding process which is preferred when using ordinary powder brands.

SIRIUS SUPRA AND SIRIUS DYESTUFFS— This card contains dyeings in two depths on bleached mercerised cotton sateen, viscose rayon and cuprammonium rayon and neutral and alkaline Rongalit C discharges on bleached mercerised cotton sateen of ninety-seven Sirius Supra and Sirius direct dyes. The amount of technical data provided is particularly comprehensive and includes graphical representation of the uptake of each dye by each type of material in presence and absence of salt and detailed information on the suitability of these dyes for application at temperatures $>$ 100°C. and by continuous dyeing methods.

ACRAFLOC WEC : ACRAFIX WEC— Acrafloc WEC an aqueous emulsion type binding agent for flock printing and Acrafix WEC a cross-linking agent for use with it.

ACRAMIN BORDEAUX FPVR— This pigment gives deep bluish reds when resin-bonded to the fibre and enables bordeaux prints of good fastness to solvents and PVC softening agents to be obtained. It is readily dischargeable. Fastness figures include— Light 6, washing (100°C.) 4–5, trichloroethylene 5, chlorine 5.

ACRAMIN ORANGE FGRL— This pigment gives bright oranges of very good fastness, including fastness to solvents, when printed or pad-dyed on cloth by the recommended resin-bonding procedure. It is suitable for use on materials subsequently to be coated with PVC. Fastness figures include— Light 8, washing (c) (203°F.) 4, chlorine (a) 5, trichloroethylene 4–5.

ACRAMIN TURQUOISE FB; ACRAMIN NAVY BLUE FB— Acramin Turquoise FB and Acramin Navy Blue FB are pigments giving bright greenish blues and navies, respectively, when resin-bonded on the fibre. Resistance to trichloroethylene and PVC softening agents is good. Fastness figures include— Turquoise FB: Light 7, washing (100°C.) 4–5; Navy Blue FB: Light 7, washing (100°C.) 5.

ACRAMIN YELLOW F5G— This pigment gives bright yellows intermediate in hue between Acramin Yellow F7G and Golden Yellow FGR when resin-bonded on the fibre. Fastness figures include— Light 6, washing (100°C.) 4–5, chlorine 5, trichloroethylene 5.

ASTRAZON YELLOW 7GLL— This basic dye gives very bright, greenish yellows when dyed or printed on polyacrylonitrile fibres, the fastness to light being particularly good even in pale depths. It is also of interest for direct printing on cellulose acetate. Fastness figures include— Dyed on polyacrylic fibre: Light 7–8, washing (b) (60°C.) 5, severe milling 4–5. Printed on acetate rayon: Light 7, washing (b) (60°C.) 4, perspiration 3.

BENZO FAST COPPER BROWN RTL— This direct dye gives dark browns of excellent fastness to light when dyed on cellulosic fibres and aftertreated on the fibre with either copper sulphate, Benzo Fast Copper Salt or Benzo Fast Copper WL. It is also of interest for direct printing and fairly good discharges can be obtained using an alkaline discharge paste containing anthraquinone. Wool and silk in mixtures with cellulosic fibres are only slightly stained. Fastness figures for a dyeing on cotton aftertreated with Benzo Fast Copper WL include— Light 7, washing (176°F.) 4, perspiration 5.

Geigy Co. Ltd.

FAST TO LIGHT ACID DYES ON WOOL PIECE GOODS— This card describes a range of fifteen acid dyes particularly recommended for dyeing gabardines, cavalry twills, tropicals and panama cloths to meet the high standard of fastness to light and perspiration. Twenty-four dyeings including greys, fawns and stone colours predominant in this trade are also shown.

IRGALAN NAVY BLUE 2GL— This neutral-dyeing metal-complex dye gives full navies on wool, polyamide fibres and silk. In dyeing behaviour and fastness characteristics it is comparable with the other dyes in this class. Dyeings on silk are of special interest because of their very good fastness to washing, water and perspiration. Fastness figures on wool include— Light 6–7, washing (b) 5, severe milling 4–5.

Imperial Chemical Industries Ltd.

TECHNICAL INFORMATION LEAFLETS— *Dyehouse No. 380. Vulcafor Fast Yellow 2GS in Polythene*— Under certain conditions bloom may develop on polythene materials coloured with this pigment. Polymon Yellow 6GS and Pure Primrose Chrome L6GS are satisfactory alternatives.

Dyehouse No. 382. Procion Dyestuffs: Continuous Dyeing of Woven Cellulosic Fibres. Supplement No. 2— The most reactive of the Procion range may be applied to cellulosic fibres using a pad (Procion dye + bicarbonate)–steam–wash sequence. Where deep colours are required partial or complete drying prior to steaming is recommended since the efficiency of the process is increased thereby.

Dyehouse No. 387. Procion Dyestuffs on Leather— The reactive dyes are of interest for dyeing leather, giving great brilliance and very good fastness to light, wet treatments, and solvents. They penetrate well and the depth of colour throughout the skin is unusually uniform giving very good fastness to buffing in the case of suède leathers. Dyeing is carried out in presence of a high concentration of salt to promote aggregation of the dye and thus increase the intensity of the colour. Dyeing at 55°C. gives satisfactory depth of colour and fastness. The minimum amount of alkali should be used for fixation to give a final dyebath pH of 7. With a few exceptions, dyes may be mixed to produce a wide range of fashion colours of pale to medium depth. Vegetable and synthetic tannins when used as "mordants" considerably reduce the depth of colour obtained.

Dyehouse No. 388. The Dyeing of Acrilan. Supplement No. 3— The Production of an Azoic Black Shade— A full black of excellent fastness to washing and pleating may be obtained with Dispersol Diazo Black B and Brenthol OT. This combination is particularly useful on cloth but is also of interest on yarn, slubbing and loose fibre. A good reserve is obtained on cellulosic fibres.

Dyehouse No. 394 (Replaces No. 255). The Dyeing of "Terylene" Polyester Fibres— Supplement No. 4. Tumescal PH— Effect on Light Fastness of Disperse Dyestuffs— Data for fastness to light of dyeings of a range of disperse dyes dyed to full depth on Terylene staple yarn in presence of Tumescals PH, OP and D and no carrier, respectively, are presented. Use of Tumescal PH, in general, produces a rather greater reduction in light fastness than either of the other carriers but the effect is probably only of importance with Duranol Red X3B.

Dyehouse No. 395. Monolite Fast Red YS in Decorative Paints.

Dyehouse No 396. Procion Dyestuffs: Use as Illuminating Colours in Brentamine Fast Blue VB Resist Styles— A method is described whereby selected members of the more reactive Procion dyes may be used as coloured resists under Brentamine Fast Blue VB. The colours produced are brighter than those obtainable with vats, solubilised vats and azoics and are generally faster to light, particularly in pale depths, than those produced with azoic combinations.

Dyehouse No. 397. Methasol Dyestuffs in Cold-curing Wood Lacquers.

Dyehouse No. 398. Liming and Filling of Full-chrome Leathers— A combined ammonia/lime treatment is recommended. Using the given procedures a well-filled leather possessing full flanks and a fine, tight grain, may be produced. There is no loss of other desirable properties and the characteristic supple handle of a full chrome tannage is retained.

Dyehouse No. 402. Procion and Procion "H" Dyestuffs: Standardisation of Printing Recipes— Details of the recommended additions of urea and bicarbonate for use with a particular concentration of dye are given. These are based on bulk experience which has shown that it is possible to specify standard recipes for all members of the range without significantly affecting colour yield and fastness properties.

Dyehouse No. 403. Procion Dyestuffs: Continuous Dyeing of Cellulosic Loose Fibre and Yarns— The "pad–bicarbonate/dry" process can be applied to yarn and loose fibre provided the necessary material to effect even impregnation is available. Thus, in the case of yarn in beam form the "slasher sizer" range has been used and loose stock scouring machinery has been used for staple viscose rayon. Loose staple rayon can be padded in the form of a lap using a cold pad liquor and dye fixation effected by either dry heat at 100–120°C., or infra-red or induction heating of the impregnated fibre mass for 1 min. at 90–100°C., steaming for 1 min. at 105°C. or batching for up to 24 hr. cold or at 50–60°C. for 1–2 hr. All the available cold-dyeing Procions are suitable with the possible exception of Yellow R which "tails" in mixtures. The impregnation of loose cotton may be difficult because it is less readily wettable.

Dyehouse No. 404. Procion and Procion "H" Dyestuffs: Fixation of Prints by Dry Heat Treatment— Colours obtained with Procion dyes fixed by dry heat are very similar to and sometimes brighter than those produced by steaming and consequently this method of fixation is of interest for mixed Procion-pigment styles. The dry-heat fixation process necessitates the addition of 20% of urea to the paste for full depths. 1·5% of bicarbonate is adequate for the more reactive Procions but 1·5% of soda ash is recommended for the "H" type. 1% of Resist Salt L should be added in all cases. The more reactive type may be fixed by heating for 3 min. at 100°C. but 5 min. at 140–150°C. is needed for the less reactive dyes.

Dyehouse No. 405 (Replaces No. 266). Weathering Fastness— Vat and Azoic Dyestuffs— Natural weathering tests made in Cheshire between April and October 1957, have shown that figures based on exposure to carbon arc light in a "Weatherometer" are not fully reliable. It is considered that a satisfactory method of test has still to be found and, for the present, dyes will simply be rated as suitable, borderline and not suitable. In the recent tests, dyes in the "suitable" class were rated 6 or higher against the light fastness standards exposed simultaneously but behind glass. The full range of vat dyes has been grouped in the three categories. The number of azoic combinations suitable for weathering is exceedingly limited.

Sandoz Products Ltd.

ARTISIL COLOURS ON ACRILAN YARN— This card contains 29 dyeings on Acrilan yarn produced with single disperse dyes and mixtures of them.

BRILLIANT ALIZARINE MILLING GREEN 2GL— This neutral or weakly acid-dyeing dye gives bright greens of very good fastness when dyed or printed on wool, silk and polyamide fibres. The colours obtained are brighter and yellower in hue than those given by Alizarine Milling Green B. It may be applied to all forms of material, is stable to chrome in the dyebath and is also suitable for mélange printing.

CUPROFIX BORDEAUX CFBL: CUPROFIX PRINTING BORDEAUX CFBL 250%— This direct dye gives full bordeaux when dyed on all forms of cellulosic materials and after-treated with either copper sulphate/acetic acid, Cuprofix SL or Resofix CU. Being very soluble, it is of special interest for pad-dyeing. The concentrated brand gives prints of very good fastness to light and wet treatments. Fastness figures for a dyeing on viscose rayon aftertreated with Cuprofix SL include— Light (daylight) 6–7, washing SNV (b) (80°C.) 4, perspiration 5.

CUPROFIX YELLOW C2GL— This direct dye gives bright yellows on cellulosic fibres when aftertreated on the fibre with either copper sulphate/acetic acid, Cuprofix SL or Resofix CU. It may be used in mixtures with all other Cuprofix C dyes and dyeings are unaffected by crease-resist finishing. Fastness figures for a dyeing on cotton aftertreated with copper sulphate/acetic acid include— Light (daylight) 7, washing SNV (60°C.) 4, perspiration 3–4.

FORON BRILLIANT VIOLET BL— This disperse dye is particularly designed for dyeing polyester fibres for which it has high affinity and on which it gives bright violets of very good fastness to light and wet treatments. It may be applied either at 100°C. in presence of a carrier or at 120–130°C. It is suitable for direct printing and of interest on acrylic fibres. Fastness figures on Dacron include— Light (daylight) 7, washing SNV (60°C.) 5, gas-fume fading 5.

LANASYN BRILLIANT RED 2BL— This neutral-dyeing acid dye gives bright bluish reds on wool, silk and polyamide fibres. It may be used alone or as a brightening colour in combination with Lanasyn and milling dyes. Dyeings have excellent fastness to light and wet treatments. It is unaffected by chrome in the dyebath. It is suitable for direct printing but not for dyed grounds since although readily dischargeable the discharged areas darken heavily on exposure to light. Fastness figures for a dyeing on wool include— Light (daylight) 6–7, washing SNV (60°C.) 4–5, alkaline milling (light) 5.

LUMICREASE BLUE 2BL— This direct dye gives greenish blues on cellulosic fibres and is particularly designed for use on cotton and spun viscose rayon cloths to be crease-resisted since the very good light fastness of dyeings is unaffected by this treatment. Some fastness figures for a dyeing on viscose rayon include— Light 6–7, washing 4–5, perspiration 4–5.

NEUTROPRINT DYESTUFFS— This card contains prints on cotton of eleven mixtures of azoic coupling components and stabilised diazotised bases marketed under this name. In contrast to the Sandogen brands, the Neutroprints can

be developed in neutral steam in 10–12 min. without Sandogen Developer S. In acid steam, development is possible in 5 min. The prints have good fastness to light, washing and chlorine. They may be used for coloured effects in resist styles under aniline black or solubilised vat dyed grounds.

SANDOTHRENE GREY F-N3G— This vat dye gives olive greys of excellent fastness to light, washing and chlorine on cotton. Crease-resist finishing slightly reddens the hue of dyeings but their light fastness is slightly improved, except in the case of Everglaze finishing when it is slightly reduced. Fastness figures include— Light (daylight) 7, washing SNV (95°c.) 5, chlorine SNV (b) 5.

SANDOTHRENE YELLOW F-N2GL— This vat dye gives bright golden-yellows on cellulosic fibres. It is particularly recommended for use alone and in mixtures for dyeing yarn and cloth to withstand bleaching and repeated washing. Ultra-dispersed brands are suitable for all types of application based on pre-pigmentation with unreduced dye. Fastness figures for a dyeing on viscose rayon include— Light (daylight) 6–7, chlorine SNV (b) 4–5, washing SNV (95°c.) 5.

SANDOTHRENE GOLDEN YELLOW NGW— This vat dye gives deep golden-yellows of good fastness to light, washing and chlorine when printed on cellulosic fibres. Fastness figures include— Light 5–6, soda boiling 5, chlorine 5.

SOLAR GREY 3LBN; CUPROFIX GREY 3LBN— This direct dye gives bluish greys on cellulosic fibres. The wet fastness of dyeings is improved by aftertreatment with Cuprofix 8L. A similar improvement is obtained using Resofix CU or Sandofix WE. The hue of dyeings becomes slightly greener and their light fastness is slightly reduced by crease-resist finishing but these effects are minimised when Finish EN is used. Wool in wool–cellulosic fibre mixtures is reserved at 80°c. and only slightly stained at the boil. Acetate rayon is reserved. Fastness figures for a dyeing on viscose rayon aftertreated with Cuprofix 8L include— Light (daylight) 7, washing SNV (b) (80°c.) 4–5, perspiration SNV 4.

SANDOZOL BROWN F-RV— This solubilised vat dye gives reddish browns of good fastness on cellulosic fibres. It may be applied on the jig or winch as well as by padding. Fastness figures on cotton include—Light 7, washing SNV (95°c.) 4–5, chlorine SNV (b) 4–5.

SOLAR BROWN 2R— This direct dye (S.D.C. classification B) gives bright red-browns on cellulosic fibres. Dyeings have good fastness to light but this is impaired by crease-resist finishing. Nylon and acetate rayon are stained. Some fastness figures include— Light 5–6, washing 3, perspiration 3.

SOLAR TURQUOISE BLUE FBL; CUPROFIX TURQUOISE BLUE FBL— This direct dye gives particularly bright greenish blues of good fastness to light on cellulosic fibres. The wet fastness of dyeings is greatly improved by aftertreatment with either Cuprofix 8L or Sandofix WE. Dyeings become greener and their light fastness is reduced by crease-resist finishing but only very slightly so when after-coppered. It is of interest for dyeing silk and for direct printing. Although the dye is a copper complex, the special brand "Vulco" may safely be used on materials subsequently to be rubber-proofed. Fastness figures for an after-coppered dyeing on viscose rayon include— Light 5, washing SNV (60°c.) 2–3, perspiration SNV 5.

SULFONINE BRILLIANT RED BGN— This acid dye gives very bright reds on wool and nylon and is recommended for dyeing slubbing and yarn. Cellulosic and acetate rayon effects are unstained. Fastness figures on wool include— Light 5, washing (60°c.) 4, carbonising 5, chlorine 5.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Metal Coating of Fabrics, Plastic Films, and Paper

H. Jörder

Textil Praxis, **12**, 917–921 (Sept. 1957)

An industrial plant for the continuous coating of fabrics, films, and paper consists of four vacuum chambers set up in series. Molten metal is vaporised under a high vacuum and deposited as a fine layer (0·1–0·3 μ. thick) on the surface of the material, giving rise to high lustre and increased reflectance of heat and light. Metal-coated fabrics have decorative and industrial applications.

L.A.T.

PATENTS

Homogenising Mill

Apex Construction *BP* 789,881

Heating Continuously Moving Threads

N.V. Onderzoekingsinstituut Research *BP* 790,163

Each thread passes through a heated tube of inner diameter $< 0{\cdot}8$ mm. and which exceeds the diameter of the thread by only such an amount that the thread is caused by its transverse oscillation during its propulsion to come into contact over its entire surface with the inner wall of the tube. Helically wound springs make suitable tubes as their diameters can be varied by stretching them.

C.O.C.

Drying or Heating Flat or Loose Material

J. Kögler *BP* 790,627

Exhaust gases at high temperature and high velocity of flow, e.g. from a gas turbine or jet drive unit, are passed into a drying machine whose ducts are so arranged that the gases pass directly from the turbine or other source of supply to the blast nozzles of the drying machine. This obviates the necessity for blowers and heaters to be part of the drying apparatus.

C.O.C.

Continuous Treatment of Warps, Cloth, Paper, etc.

Wiesner-Rapp Co. *BP* 789,996

A tank consists of at least three compartments through which the material passes in succession. The guide units in each compartment can have their speeds adjusted individually while the apparatus is working, thus enabling any desired degree of tension to be imparted at any stage of processing. Treating fluid is supplied to each compartment separately.

C.O.C.

Inhibiting Corrosion of Stainless Steel by Chlorine Dioxide

FH *BP* 790,302

Corrosion of stainless steel by gaseous chlorine dioxide in presence of acid vapours is prevented by introducing into the "gas space" of the apparatus a gaseous mixture containing water, nitric acid, and an acid volatile in steam, e.g. acetic or formic acid.

C.O.C.

Tenter

Famatex *BP* 789,559

A tenter whose important parts can be cleaned and checked without difficulty and with small expenditure of time and work.

C.O.C.

Sampling Travelling Webs

J. J. Cannan *BP* 789,925

A simple device for taking samples from e.g. paper during its manufacture.

C.O.C.

Folding and Measuring Cloth

Gillet-Thaon *BP* 789,192

A folding and measuring machine has a vertically slidable table. This table has a seam detector which causes the table to lower and eject the cloth from it wherever a seam comes onto the table. By this means lowering of the table and ejecting of the folded piece of cloth are effected automatically and in correct order without the machine being stopped and without any action by the operator being needed.

C.O.C.

Dry-cleaning Plant

Baker Perkins *BP* 790,418

Plant in which the drum is constructed to give unusually efficient and rapid initial impregnation of the goods with solvent, more effective distribution of the solvent through

the load and quicker and complete extraction of the liquid and/or vapour solvent after use. C.O.C.

Apparatus for Use in Preparing Colour-separation Photographic Negatives
Hunter-Penrose *BP* 790,683

New Developments in Sodium Chlorite Bleaching (VII p. 320)
Squeegee for Screen Printing (IX p. 323)
Compressive Shrinking (X p. 326)

II—WATER AND EFFLUENTS

Behaviour of Sulphides and Sulphur Dyes in Effluents
M. Kehren and H. Denks
S.V.F. Fachorgan., **12**, 138–153 (March), 492–498 (July 1957)

Purification of effluents was investigated under laboratory conditions. Best results were obtained when the aeration treatment was preceded by souring with commercial hydrochloric acid or a mixture of carbon dioxide and air. The more soluble sulphur dyes were precipitated by the addition of ferric chloride at pH 5·5. L.A.T.

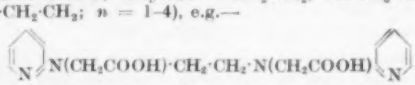
III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

PATENTS

Dipyridyl Aliphatic Alkylene Polyamine Polyacids — Chelating Agents
Dow Chemical Co. *USP* 2,751,390

Compounds of formula—

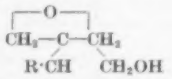
(A = CH_2COOH or a higher homologue acid; R = aliphatic chain of 1–12 C; alkylene = $CH_2{\cdot}CH_2$, $CH{\cdot}CH_3{\cdot}CH_2$ or $CH_2{\cdot}CH_2{\cdot}CH_2$; n = 1–4), e.g.—



are water-soluble chelating agents yielding extremely stable Ni and Co complexes. C.O.C.

Surface Active Polymeric Trimethylene Oxide Derivatives having Polyether Side Chains
FBy *BP* 789,415

Polymers of trimethylene oxide alcohols of formula—



(R = H, hydroxyl, alkyl, or a hydroxyalkyl radical) when treated with an alkylene oxide are used as wetting, dispersing, levelling or cleansing agents. They have good antistatic properties. C.O.C.

Knitting Lubricants for Cellulose Acetate or other Organic Derivative of Cellulose
Celanese Corp. of America *BP* 789,716

A mixture of eicosane and an amine salt of an acid phosphate of a higher fatty alcohol is an excellent lubricant for acetate rayon yarns during knitting. It does not age, does not corrode black iron either in presence or absence of water, has excellent antistatic properties and is readily removed by washing in water. C.O.C.

Cleansing Compositions for Surfaces contaminated with Heavy-metal Compounds
Brentford Soap Co. *BP* 790,306

An aqueous cleansing cream for removing heavy metal compounds, particularly radioactive compounds, from clothing, apparatus and the human skin comprises an alkali metal or ammonium or substituted ammonium (including alkylolamine) salt of a polyamino-polycarboxylic acid (or nitrilotriacetic acid) sequestering agent or an alkaline earth metal complex thereof, water and a water-soluble polymer which yields solutions of high viscosity. The composition must contain no derivative of a fatty acid amide of > 7 C. C.O.C.

Organosilicone Emulsions as Textile Finishes
Midland Silicones *BP* 790,038

An oil-in-water emulsion made up of (1) 0·5–20·0% of a hydrocarbon solvent-soluble organopolysiloxane containing on the average 0·005–1·0 silicon-bonded H atoms per Si atom, and (2) 80–99·5% of an aqueous solution of a Ti or Zr compound of strength such that the emulsion contains 0·5–15·0% of metal on the weight of the polysiloxane, is used to render textiles water-repellent. The emulsion is highly stable with respect to hydrogen evolution and storage. C.O.C.

Electron-microscopic Examination of Detergents (XIV p. 327)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Preparation of Amines and Hydrazo Compounds
P. M. G. Bavin
Canadian J. Chem., **36**, 238–241 (Jan. 1958)

The reduction of nitro compounds to amines by ethanolic hydrazine and palladised charcoal probably proceeds through the nitroso and hydroxylamine derivatives. This reagent is useful for the reduction of azo to hydrazo compounds. W.R.M.

Preparation of Benzidine using Aliphatic Alcohols as Reducing Agents
D. F. Kutepov and V. E. Reinshtein
J. Appl. Chem. U.S.S.R., **30**, 1108–1111 (July 1957)

When to the boiling mixture of 50 g. NaOH and 75 ml. CH_3OH 123 g. of nitrobenzene is added during 2 hr., and boiling continued for further 3 hr., or until the smell of the nitrobenzene disappears, 96 g. azoxybenzene separates equivalent to a 97% yield, and from the aqueous filtrate 33 g. H·COOH can be recovered. The reduction of the azoxybenzene so produced with 90 g. of Zn dust at 80°c. results in the formation 87·2 g. hydrazobenzene and 3·73 g. aniline. The separated hydrazobenzene on treatment with HCl gives an 83% yield of benzidine. The reduction of the azoxybenzene can also be effected by passing H_2S through its solution in a mixture of C_2H_5OH and aq. NH_4OH. Instead of CH_3OH and C_2H_5OH, ethylene glycol can be used. The method was found to be satisfactory for large-scale work and can also be employed for the production of benzidine homologues. T.Z.W.

Physical Properties of Aminoazobenzene Dyes. V—The C_s/A_s Ratio
E. Sawicki
J. Org. Chem., **22**, 621–5 (1957): *Chem. Abs.*, **52**, 282 (10 Jan. 1958)

Investigation of the tautomerism of 73 azobenzene derivatives in 50% alcoholic acid solution is described. The reproducible, simply-obtained C_s/A_s ratio gave a rough idea of the ratio of C (proton goes to β-N) to A (proton goes to amino N) tautomers present in the acid solution. This C_s/A_s ratio should be very useful in determining the structures of unknown azo dyes. It is correlated with basicity, resonance, inductive, steric, and intra- and intermolecular H bonding effects. Approximately 100 spectra (310–600 mμ) in 50% alcoholic acid are given. Most of the C_s/A_s values were obtained at a HCl normality of 1·0 or 1·2. At this acidity most 4-aminoazobenzene dyes show slight change in the C_s/A_s ratio with change in normality of the acid. The ideal would be to obtain C_s/A_s values at the lowest normality at which 100% of the monocationic salt is present; 1·0–1·2 is close to this. The pK_a, C band in mμ, A band in mμ, HCl normality and C_s/A_s for the 73 azobenzene derivatives are given. C.O.C.

Physical Properties of the Aminoazobenzene Dyes. VII—Absorption Spectra of 4-Aminoazobenzene Dyes in Ethanol
E. Sawicki
J. Org. Chem., **22**, 915–919 (1957): *Chem. Abs.*, **52**, 875 (25 Jan. 1958)

A study of the visible absorption spectra of approx. 60 azobenzene derivatives in 95% alcohol. Of particular interest was the effect of various substituents on the long-wave band association with a zwitterionic resonance structure. Increasing shift towards the visible was shown

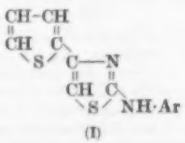
by 4-substituted azobenzenes with the following substituents: H < CH_3 < $NHCOCH_3$ < OH < SCH_3 < NH_2 < $N(CH_2CH_2Cl)_2$ < $NHCH_3$ < NHC_2H_5 < $N(CH_3)_2$ < $N(C_2H_5)_2$. Substitution of electron acceptor groups in the 4′-position of 4-aminoazobenzene dyes caused increasing shift toward the visible in the order: H < C_6H_5 < SCN < $CH{:}CH_2$ < CH_3CO < $N{:}N{\cdot}C_6H_5$ < NO_2. With 4-dialkylaminoazobenzene dyes containing either a NO_2 or CH_3CO group at the negative end of the molecule, there was gradual shift toward the visible in the order 3′ < 2′ ≪ 4′. Presence of alkoxy, methylthio or NH_2 at the negative end of the molecule had very little effect on the λ_{max} in 95% alcohol. In naphthalene dyes, e.g. 4-phenylazo-1-naphthol, λ 409 mμ as compared with 4-hydroxyazobenzene, λ 349 mμ, the bathochromic shift is postulated to be caused by the relatively lower energy of the α-naphthoquinone excited state structure compared with the p-benzoquinone excited state structure of 4-hydroxyazobenzene. The relative intensities of 2 adjacent bands in Cl, CH_3O, CH_3S, and NH_2 derivatives of 4-dialkylaminoazobenzenes are known to be solvent-dependent. In aqueous alcohol 2′-amino-4-dimethylaminoazobenzene showed evidence of spectral fine structure that appeared to be absent in the other compounds. On the basis of this structure it is suggested that this compound existed mainly in a structure which contained a 5-membered ring involving an intramolecular H bond between the amino H and the β-azo H. The structure involving a 6-membered ring contained an intramolecular H bond between the amino H and the α-azo N was also believed to be present. Syntheses of 10 azo dyes hitherto unrecorded are given. C.O.C.

2:4-Diaminothiophen; the Diazotisation Reaction of 2:4-Diaminothiophen, and its Azo Derivatives
N. I. Putokhin and A. N. Sorokin
Sbornik Nauch. Trudov, Kuibyshev. Ind. Inst. im. V. V. Kuibysheva 1955, No. 5, 261–270: *Chem. Abs.*, **51**, 16419 (10 Nov. 1957)

Nitration of 2-nitrothiophen followed by reduction with Sn and HCl gave 2:4-diaminothiophen (I). Treatment of I with nitrous acid gave the tetrazo compound, which was coupled with phenolic and amino coupling components to give disazo dyes. β-Naphthol for instance gives an alkali-soluble dye giving orange on wool. E.S.

Preparation of 2-Arylamino-4-(2′-thienyl)-thiazoles and their Azo and Mercurated Derivatives
G. N. Mahapatra and M. K. Rout
J. Indian Chem. Soc., **34**, 653–659 (Sept. 1957)

The title compounds (I) have been prepared by condensing methyl 2-thienyl ketone with phenylthiourea, its o-, m-, and p-methyl-carboxy, and -chloro derivatives, and α- and β-naphthylthiourea. They couple with diazotised sulphanilamide in the 5 position of the thiazole nucleus. Mercuration with mercuric acetate takes place in the aryl nucleus.



(I)

C.H.R.

Triarylmethane Compounds as Redox Indicators in the Schoenemann Reaction. III—Dyes and their Spectra
G. A. Grant, R. Blanchfield, and D. M. Smith
Canadian J. Chem., **36**, 242–250 (Jan. 1958)

Triarylmethane dyes were made by varying the substituents in the thiophene ring of the dye [4-(*p*-dimethylamino-α-thienylbenzylidene)-2:5-*cyclo*hexadiene-1-ylidene] dimethylammonium chloride. The spectra of zinc salts are similar to that of the dye formed in the Schoenemann reaction when the parent triarylmethane is used as indicator. Absorption bands at 475 mμ. and 625 mμ. are unaffected by pH in the range 2·4–6·4 but are hypsochromically shifted when the pH is lowered to 0·5. Substitution of 5-nitro and 5-acetamido groups in the thiophen ring results in the largest bathochromic and hypsochromic shifts respectively. Interpretation in terms of theories relating colour and constitution is attempted. W.R.M.

Synthesis of Cyanine Dyes from *p*-Diethylaminobenzaldehyde—VII
M. Q. Doja and J. C. Banerjee
J. Indian Chem. Soc., **34**, 599–605 (Aug. 1957)

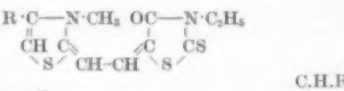
p-Diethylaminobenzaldehyde has been condensed with the methiodide derivatives of 4-*p*-tolyl- and 4-(*p*-chloro-, *p*-bromo-, and *p*-iodo-phenyl)-2-methylthiazoles, 4:5-diphenyl-2-methylthiazole, and 2:5-dimethyl-4-phenylthiazole. The extra sensitisation imparted by these groups in the 4 position is in the order *p*-iodophenyl > *p*-bromophenyl > *p*-chlorophenyl > *p*-tolyl > phenyl > methyl. Substitution of a methyl group in the 5 position has a greater effect than that in the 4 position. These cyanine dyes give reddish browns to pinks on cotton, silk and wool. C.H.R.

Cyanine Dyes—I
B. Das and M. K. Rout
J. Indian Chem. Soc., **34**, 505–508 (July 1957)

Cyanine dyes containing thiazole groups, such as 4-phenyl-, 4-*p*-alkoxyphenyl-, 4-*p*-bromophenyl-, and 4-*p*-nitrophenyl-2-methylthiazoles and 2-methylbenzothiazole, have been prepared by condensing the corresponding methyl quaternary salts with ethyl orthoformate or with acetanilidovinyl compounds such as diphenylformamidine. C.H.R.

Photographic Sensitisers. I—*mero*Carbocyanines
B. K. Patnaik and M. K. Rout
J. Indian Chem. Soc., **34**, 543–547 (July 1957)

*mero*Carbocyanines containing thiazole groups have been prepared by condensing 4-phenyl and 4-(substituted)-phenyl-2-methylthiazole methiodide compounds with diphenylformamidine in acetic anhydride to give the corresponding 2-(2′-acetanilidovinyl) compounds, which on treatment with 3-ethylrhodanine form the *mero*carbocyanines of general formula—



C.H.R.

***mero*Cyanines—I**
B. K. Patnaik and M. K. Rout
J. Sci. Ind. Research (India), **16B**, 253–256 (1957): *Chem. Abs.*, **52**, 368 (10 Jan. 1958)

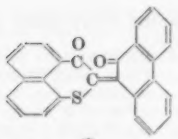
Condensing 2-methylthiazole methiodides containing a reactive methyl group with CH_3COCl in cold pyridine suspension results in formation of pseudo ketones which when condensed with a reactive oxomethylene compound yield dimethin *mero*cyanines having substituents in the dimethin bridge. Thus 4-phenyl-2-methylthiazole methiodide treated with CH_3COCl in pyridine at 0°c., then heated in a water bath and the pyridine removed gave 2-acetylmethylene-3-methyl-4-phenylthiazoline which on refluxing with acetic anhydride and then removing the acetic anhydride *in vacuo* and treating the residue with ether yields the bluish violet 5-{[3-methyl-2(3*H*)-4-phenylthiazolylidene]*iso*propylidene} rhodanine. C.O.C.

New Flavylocyanines and *mero*Cyanines
T. Fotakis
Chim. et Ind., **78**, (3 bis), 98 (Sept. 1957)

New unsymmetrical flavylocyanines have been prepared. By working with flavylium perchlorate in acetic anhydride or glacial acetic acid (with prolonged boiling in the latter case) it is possible to obtain the symmetrical diflavylomonomethin. The values of λ_{max} of the new monomethins have been measured, and their deviation from the arithmetic mean has been calculated. With most of the new monomethins this deviation is toward shorter wavelengths according to the basicity of the end rings of the unsymmetrical cyanine. With others the rule does not appear to hold. C.J.W.H.

Indigoid Dyes. XXI—1:8-Naphthapenthiophenphenanthrene-indigos
P. C. Dutta and S. K. Roy
J. Indian Chem. Soc., **34**, 660–662 (Sept. 1957)

1:8-Naphthoxypenthiophen has been condensed with phenanthrene and its nitro, dinitro, chloro, and amino derivatives to give dyes of general formula I. They are much deeper in colour than the corresponding 2:3-naphthathiophen products, but are unsuitable for dyeing cotton because of their sparingly soluble leuco compounds.



(I) C.H.R.

Zolon Red and the Zolon Red–Silver Complex
G. F. Svatos and J. Goldenson
J. Org. Chem., **21**, 1171–3 (1956): *Chem. Abs.*, **52**, 875 (25 Jan. 1958)

Absorption spectra of Zolon Red and Zolon Blue show maximum absorption at 522 and 620 mμ. respectively, while in acid solution both absorb strongly at 430 mμ. In the infrared range, the red dye absorbs at 5·96 mμ. corresponding to C:O and the blue dye at 5·90 mμ.; only the blue dye has a band corresponding to OH and NH. Only Zolon Red forms a 1:1 coordination compound with Ag^+. C.O.C.

PATENTS

all-*trans*-4:4′-Disubstituted Carotenoid Compounds — Food Dyes
F. Hoffmann–La Roche & Co. *BP* 790,614

Acetylene is condensed in a metal-organic reaction with 8-[2′:6′:6′-trimethylcyclohexen-(2′)-ylidene-(1′)]-2:6-dimethyloctatrien-(2:4:6)-al-(1) and the resulting 1:18-di[2′:6′:6′-trimethylcyclohexen-(2′)-ylidene-(1′)]-3:7:12:16-tetramethyl-8:11-dihydroxyoctadecahexaen-(2:4:6:12:14:16)-ine-(9) chlorinated or brominated. Both the halogenations in the resulting 4:4′-di(chloro- or bromo)-15:15′-dehydro-β-carotene are replaced by hydroxyl or acyloxy groups and, if desired the 4:4′-(dihydroxy or acyloxy)15:15′-dehydro-β-carotene obtained is catalytically hydrogenated to reduce the triple to a double bond and the 15:15′-monocis 4:4′-di(hydroxy or acyloxy)-β-carotene so produced isomerised to yield the corresponding all-*trans* 4:4′-di(hydroxy or acyloxy)-β-carotenes.

BP 790,615

The 4:4′-di(chloro or bromo)-15:15′-dehydro-β-carotene obtained as above is either (1) hydrogenated to convert the triple bond into a double bond and the resulting monocis 4:4′-dihydroxy-β-carotene oxidised so as to convert both hydroxyl groups to keto groups, or (2) oxidised to convert both hydroxyl groups into keto groups and, if desired, the resulting 4:4′-diketo-15:15′-dehydro-β-carotene hydrogenated to convert the triple bond into a double bond.

BP 790,616

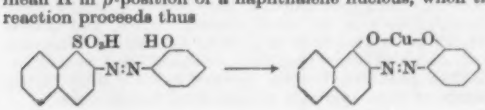
Describes the steps necessary to produce the 4:4′-dibromo (or dichloro)-15:15′-dehydro-β-carotene mentioned above. C.O.C.

Violet and Blue Metal(Chromium and Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc.
ICI *BP* 790,261

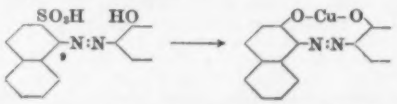
The complexes containing 1 atom of Cr or Co to 2 mol. of azo compounds made by coupling a naphthalene-2-diazo-1-oxide having a sulphonamide group in the 5, 6, or 7 position with 5-chloro- or 5:8-dichloro-1-naphthol (I) dye wool, nylon, etc., violet and blue from neutral or weakly acid baths. The diazo compounds may be made by e.g. (*a*) oxidation of a soln. of a diazotised 2-naphthylamine-5(or 6 or 7)-sulphonamide with e.g. a ferricyanide, or (*b*) diazotisation of a 1-nitro-2-naphthylamine-5(or 6 or 7)-sulphonamide. Thus naphthalene-2-diazo-1-oxide-5-sulphonamide is coupled with I in aq. Na_2CO_3, and the monoazo compound, suspended in aq. ethylene glycol, is refluxed with chromium triacetate. The product dyes wool and nylon blue. E.S.

Metal(Copper)-complex Azo Dyes from *o*-Hydroxy-*o*′-sulphoazo Compounds
FBy *BP* 790,386

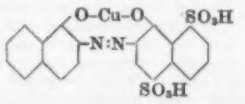
By treating *o*-hydroxy-*o*′-sulphoazo compounds, having in the other *o*′-position a non-chelating substituent X, with a copper salt and a suitable oxidising agent, the sulpho groups are eliminated with formation of the Cu complexes of the *oo*′-dihydroxyazo compounds. X may also mean H in β-position of a naphthalene nucleus, when the reaction proceeds thus



If X stands for the 9-position of a naphthalene nucleus the reaction proceeds as follows—



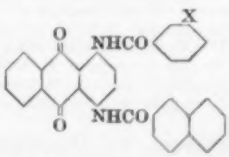
Thus the monoazo compound 2-naphthylamine-1-sulphonic acid → 1-naphthol-4:8-disulphonic acid is stirred in aq. $CuSO_4$ and 3% aq. H_2O_2 run in at 50°c., to give the complex—



without using the carcinogenic β-naphthylamine. It may be made into the metal-free *oo*′-dihydroxyazo dye by treatment with acid. E.S.

Red Anthraquinone Vat Dyes
CFM *BP* 789,120

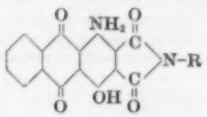
Red vat dyes of good fastness are



(X = Cl or Br). They are made by (1) condensing 1-amino-4-(β-naphthoylamino)-anthraquinone with e.g. *m*-chlorobenzoic acid or (2) condensing 1-(*m*-chlorobenzoylamino)-4-aminoanthraquinone with β-naphthoic acid, or (3) condensing 1:4-diamino- or *leuco*-1:4-diaminoanthraquinone in two stages with the above acids. Thus, monochlorobenzene (300), 1-amino-4-(β-naphthoylamino)-anthraquinone (20) and *m*-bromobenzoylchloride (22) are heated 12 hr. at 120°c. After cooling the dye is filtered, washed and dried. The dyes have greater affinity for the fibre than the 1:4-dibenzoylaminoanthraquinones and the 1:4-di-β-naphthoylaminoanthraquinones described in *GP* 225,232 and 432,579 respectively. E.T.

Blue to Violet Anthraquinone Disperse Dyes
DuP *USP* 2,749,354

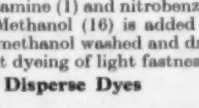
Blue to violet dyes for polyester and polyacrylic fibres of good light fastness are of formula—



(R = alkoxyalkyl radicals, e.g. 3-methoxypropyl, 2-methoxyethyl, etc.). They are prepared by reacting an aliphatic amine with 1-amino-4-hydroxy-2:3-anthraquinone dicarboxylic acid or its anhydride. Thus 1-amino-4-hydroxyanthraquinone dicarboxylic acid anhydride (2), 3-methoxypropylamine (1) and nitrobenzene (6) are heated 2 hr. at 120°c. Methanol (16) is added at 25°c. and the product filtered, methanol washed and dried. The product gives bluish-violet dyeing of light fastness 7. E.T.

Anthraquinone Disperse Dyes
ICI *BP* 790,082

Known blue disperse dyes of high fastness to gas fumes and of good affinity for cellulose esters and superpolyesters are



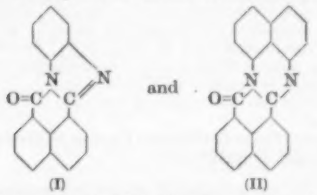
(R = $[OCH.CH_2]_nOH$ or $-CH_2O[CH_2{\cdot}CH_2]_{n'}Z$; n = 1–4; n' = 1–3; Z = H or $Alk_{n'}$). According to the present invention, dyes of similar fastness but improved affinity

are obtained by treating a 5-nitro-4-anilino-1:8-dihydroxyanthraquinone with HCHO in 80–85% H_2SO_4. Thus, paraformaldehyde (40) is added to 80% H_2SO_4 (600) and the mixture is stirred 30 min. at 15–20°c. 5-Nitro-4-anilino-1:8-dihydroxyanthraquinone (60) is added and the melt stirred at 20–30°c. for 16 hr. Drowning into ice (3000) and water, filtration and washing neutral gives a blue dye. A further advantage is that the use of costly substituted anilines required to make the earlier products is avoided. E.T.

Production of Naphthoylenearyliminazole and Naphthaloperinone Dyes on the Fibre

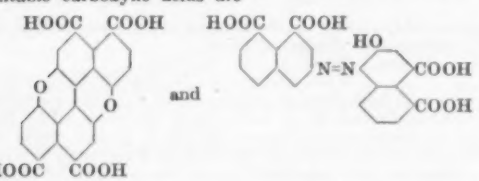
FBy *BP* 789,310

Textile fibres are coloured by printing or padding processes using compositions containing (*a*) a carboxylic acid having at least two COOH groups in peri positions, (*b*) an *o*-diamine or peridiamine, and (*c*) an acid condensing agent or its NH_4 salt. Dyes which would normally be practically insoluble are formed in the fibre by short heat treatment. The dyes formed are of two classes—



(I) (II)

(I = naphthoylenearylimidazoles from *o*-diamines; II = naphthaloperinones from peridiamines). Examples of suitable carboxylic acids are



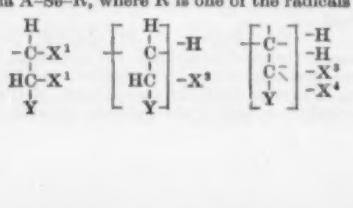
(III) (IV)

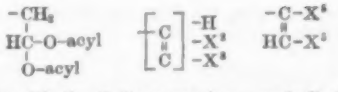
the latter being formed by coupling a diazotised amine with hydroxynaphthalene-1:8-dicarboxylic acid. In one example, 1:4:5:8-naphthalenetetracarboxylic acid (3·04) is dissolved in water (20) and 25% NH_4OH (3); thiodiglycol (4), diglycolmonomethylether (4), *o*-phenylenediamine (4·3), 40% aq. NH_4 lactate (21·4), 65 : 1000 tragacanth thickener (35), and water (5·26) are stirred in successively. The paste is printed on cotton, viscose or acetate rayon, dried and the dye produced by acid or neutral steaming or heating at 120–30°c. Clear reds of excellent fastness are obtained after soaping. The dyes thus produced on the fibre are similar to the vat dyes described in *GP* 430,632. E.T.

Addition Compounds containing Selenium— Disperse Dyes

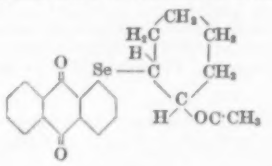
Ciba *BP* 788,725

Dyes for dyeing or printing cellulose acetate or polyamide fibres are made by reacting A–Se–O–Acyl with an unsaturated organic compound (A = aromatic res. which is, preferably, vattable, e.g. anthraquinone). The selenium-containing starting material is obtained by (1) reacting A–Se–OAlk with an acid, or (2) reacting A–SeHal with a salt of an acid. (For preparation of anthraquinone-1-selenic acid methyl ester, see *Helv. Chim. Acta*, **35**, 849 (1952).) As unsaturated compounds, those containing >C=C< are preferred, e.g. ethylene, vinyl acetate, *iso*butylene, butadiene, styrenes, etc. The use as solvent of e.g. glacial acetic acid is advantageous as it allows the two stages, i.e. (*a*) preparation of A–Se–O–Acyl and (*b*) reaction with unsaturated compound, to be carried out without intermediate separation. The final products are of formula A–Se–R, where R is one of the radicals





(both X^1's with the C–C group give a *cyclo*alkyl radical; X^2 = phenyl or Alk; X^3, X^4 = Alk; both X^5's with C = C group give a pyrane radical; Y = acyl or OH group). Thus, anthraquinone-1-selenenic acid methyl ester (34·5) is boiled in glacial acetic acid (1000 cc.) to give the 1-selenenyl acetate. *cyclo*Hexene (10) is added, the whole is boiled 1 hr., cooled, filtered, and a large amount of water added to the filtrate. The resulting precipitate is filtered, water washed, and dried *in vacuo* at 80°c. and consists of

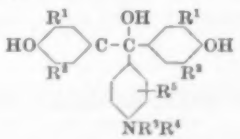


m.p. 169°c. E.T.

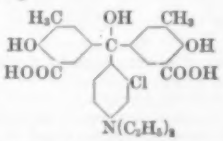
Dyes for Antihalation Layers

Agfa AG für Photofabrikation *BP* 790,023

Dyes of formula—



(R^1 = H, subst. or unsubst. Alk, hydroxy, alkoxy, aralkyl or Hal; R^2 = H, Alk, NO_2 or COOH; R^3 = subst. or unsubst. Alk or Ar; R^4 = subst. or unsubst. Alk; R^5 = H, Hal or Alk), e.g.

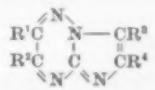


are excellent antihalation dyes both from their antihalation properties and their effect on the photographic material during storage and processing. C.O.C.

Fluorescent Pigments

Industria Chimica Profarmaco *BP* 789,850

Compounds of formula—



(R^1, R^2, R^3 and R^4 = H, Alk, Ar or Ar substituted by NO_2) are obtained by heating together appropriate 3-imino-1:2:4-triazines and *a*-halogenocarbonyl compounds. The products are useful as luminous pigments and in solution show intense fluorescence. They are highly heat-resistant, chemically inert and resistant to light and weathering. They are usually yellow, melt at high temperatures, are insoluble in water, alkali and acid, but soluble in many organic solvents. C.O.C.

Alkali-metal Ferrocyanides and Ammonium Sulphate— Intermediates for Iron Blue (C.I. Pigment Blue 27)

Imperial Paper & Color Corpn. *BP* 790,885

An alkali metal hydroxide and ferrous hydroxide are made into an aqueous slurry and treated with coke oven gas to produce an alkali metal cyanide. The gas not absorbed by the slurry is passed into an aqueous solution of ferrous sulphate to absorb the ammonia and form ferrous hydroxide for use in the first operation and ammonium sulphate. The ferrocyanide, ammonium sulphate and ferrous hydroxide are produced in amounts close to those needed for the manufacture of the various types of Iron Blues. C.O.C.

Calcium Carbonate, C.I. Pigment White 18
George Forbat & Co. and Charles Goldrie, Foucard & Son *BP* 790,073

Eggshells are washed, if necessary the protein content removed, e.g. with hot caustic soda, dried, and then powdered. The product is particularly suitable as a pigment for cosmetic or pharmaceutical purposes. C.O.C.

Zinc Ferrite Pigment
Columbian Carbon Co. *BP* 790,949

Ferric oxide and zinc oxide are made into an aqueous slurry with 0·4–0·6% by wt. excess Fe_2O_3 over molecular proportions. The slurry is dried, heated in presence of a volatile chloride catalyst, e.g. $ZnCl_2$, to yield a zinc ferrite which is readily reduced to a fine powder of strength and yellowness of tint superior to hitherto known zinc ferrites. It is exceptionally stable to heat, alkali, and acids, is non-ferromagnetic and free from water-soluble salts. C.O.C.

Hectograph Black (V this page)
Crystal Violet for Shading Blacks for Carbon Paper and Hectograph Inks (V this page)
Dyeing Polyacrylonitrile Fibres and Films (VIII p. 322)
Colour Photography (IX p. 323)
Fluorometric Determination of Thallium with Rhodamine B (C.I. Basic Violet 10) (XIV p. 327)
New Colour Reactions of Phthaleincomplexone (XIV p. 327)

V—PAINTS; ENAMELS; INKS

PATENTS

Hectograph Black
General Aniline *USP* 2,752,254

A mixture of Crystal Violet (C.I. Solvent Violet 9) (35–45 parts by wt.), Chrysoidine (C.I. Solvent Orange 3) (40–45), and Rhoduline Blue (C.I. Basic Blue 1) (15–20) used in hectograph ink yields prints which do not vary in colour from first to last. C.O.C.

Crystal Violet for Shading Blacks for Carbon Paper and Hectograph Inks
W. G. Clarke and W. G. Drautz *USP* 2,752,255

Subjecting an aqueous dispersion of Crystal Violet (C.I. Solvent Violet 9) to atmospheric drum drying to yield a product of $< 2\%$ moisture content results in no change in the crystal form of the dye. The low moisture content of the product makes possible production of very low viscosity compositions, particularly hectograph inks coloured with a black dye mixture having Crystal Violet as one of its components. The process is also applicable to dye mixtures containing $\not< 30\%$ by wt. of Crystal Violet. C.O.C.

Emulsion Gloss Paints
Petrochemicals *BP* 790,060

A paint which yields glossy films and has satisfactory application and flow properties consists essentially of synthetic latex, pigment, and protective colloid. The amount of protective colloid is 0·5–4·5 mg. per sq.in. of the total surface area of the pigment. The total volume of pigment is $\not> 35\%$ of the total volume of non-aqueous constituents. C.O.C.

VI—FIBRES; YARNS; FABRICS

Thermodynamic Relations between Stresses, Deformations, and Moisture Absorption
J. W. S. Hearle
Text. Research J., **27**, 940–945 (Dec. 1957)

A new derivation of the relation between moisture absorption, swelling, and applied stresses has been given and has been used to obtain the equations applicable to textile systems. They are strictly valid only under reversible conditions. Some applications of these equations have been suggested. They may also be of value in dealing with other problems, particularly in relation to the dimensional stability of material under changing moisture conditions, which is sometimes a serious defect in use. S.B.D.

Improved Process for Cotton Decrystallisation
H. J. Janssen, C. H. Haydel, J. F. Seal, and H. L. E. Vix
Text. Research J., **27**, 622–625 (Aug. 1957)

Ice-cold water was used on both laboratory and pilot-plant scales to extract residual monoethylamide reagent from decrystallised cotton materials. The use of cold water retained the high degree of decrystallisation achieved and further retained the cellulose I crystal lattice of native cotton in the remaining crystalline areas. Advantages of this cold-water extraction process compared with the use of organic solvents are enumerated. S.B.D.

Bacteriological Studies on Cottons
A. N. J. Heyn
Text. Research J., **27**, 591–603 (Aug. 1957)

Experimental data are presented on the occurrence of cellulose-decomposing bacteria on raw cotton. From all samples of field cotton investigated, cellulose bacteria could be isolated starting shortly after the opening of the boll. All species belong to the order *Myxobacteriales*, of which all representatives known to decompose cellulose in the total six species were found to occur. Some of these bacteria are common inhabitants of the soil; a few others have been rarely observed in the U.S.A. The decomposition of raw cotton fibre, under the influence of some of these bacteria, is studied in the laboratory. A literature review on cellulose-decomposing bacteria is added. S.B.D.

Microscopic Observations on Cotton Fibres subjected to Enzymatic Degradation
P. B. Marsh
Text. Research J., **27**, 913–916 (Nov. 1957)

Experiments resulting in the transverse cracking and fragmentation of the cotton fibres are compared with earlier work which resulted in helical cleavage. S.B.D.

Effect of Cellulase on the Degree of Polymerisation of Cellulose and Hydrocellulose
E. T. Reese, L. Segal, and V. W. Tripp
Text. Research J., **27**, 626–632 (Aug. 1957)

On acid hydrolysis of cotton, the D.P. of the insoluble residue falls rapidly to a low level (levelling off of the D.P.). Continued hydrolysis results in further losses in weight, but the D.P. and the micelle dimensions remain unchanged. It is suggested that at the levelling off of the D.P. the individual micelles disappear, i.e. further action of acid yields only soluble fragments. The present investigation was undertaken to compare the action of enzymes on the micelles with that of acids. The study was broadened by the inclusion of hydrocelluloses from cottons treated in various ways, and further extended to include the parent materials from which the hydrocelluloses were prepared. S.B.D.

Size of the Intermicellar Spaces and Capillaries in Jute Fibres as revealed by X-Ray Analysis
S. K. Chowdhury
Text. Research J., **27**, 935–939 (Dec. 1957)

The dimensions of the intermicellar regions and capillaries in raw jute fibres have been estimated from the sizes of the colloidal gold and silver particles deposited in the fibre under different conditions. It has been inferred that the dimensions of the colloidal particles indicate only the dimensions of the capillaries after they have been enlarged by swelling or by the deposition process itself. The size of the particles determined is of the order of 100A.; it has been pointed out that they remain within the wider capillaries present in jute fibre because the intermicellar region is too small to accommodate these particles. Unlike ramie, in jute fibres treated for a short time in weaker soln. the particles cannot form even in these capillaries. They form within much wider capillaries (about 200A.), partly because the smaller capillaries are blocked by the non-cellulosic materials, especially lignin, and partly because the swelling of ramie fibres is faster than that of jute fibres. This has been corroborated by the fact that the dimensions of these dispersoids in holocellulose increase to 126A. S.B.D.

Native Hemp, Jute, and Kapok Celluloses
T. E. Timell
Text. Research J., **27**, 854–859 (Nov. 1957)

The general chemical composition of untreated fibres of hemp, jute, and kapok has been studied, and the results have been compared with the composition of the corresponding α-cellulose and of the cellulose nitrates obtained

by direct nitration of the original materials. After correction for non-glucose sugar residues, the data indicated the presence of approx. 80, 60, and 40% cellulose respectively in the native fibres. Unlike the hemp and jute, the kapok cellulose could not be nitrated to completion. No evidence was obtained for any association between α-cellulose and xylan in jute. The average D.P. of the nitrates was 4800 for hemp, 4700 for jute, and 3300 for kapok cellulose, the first two values being the same as those found previously for native cotton and flax celluloses. The mol.-wt. distributions contained only one max. and were symmetrical for hemp and jute, the curve for kapok having a slight right-hand skewness. The results were compared with earlier data for other bast and seed fibres. S.B.D.

Relationship of Experimentally Evaluated Lateral-order Distribution to the Skin–Core Effect of Viscose Rayon
Y. Tsuda and S. Mukoyama
Text. Research J., **27**, 945–949 (Dec. 1957)

The lateral-order distributions of experimental rayons spun in baths of various compositions are evaluated using the method of fractional dissolution of the methanolised cellulose. They are compared with the skin–core effect of cross-section which is characteristic of the structure of viscose rayon. S.B.D.

Fine Structure of Keratin
E. H. Mercer
Text. Research J., **27**, 860–866 (Nov. 1957)

The results of work using the electron microscope with thin sections of keratinous fibres, both before and after extraction of the keratin, are described. Both the cortex and the cuticle are cellular, but the normal constituents are in a dried and altered form with intracellular deposits of keratin. On extracting the keratin, the cell membranes, nuclei, and certain cytoplasmic residues are left behind. The cortical keratin is fibrous, consisting of fine filaments (ca. 60A. in diameter) cemented together into fibrils, which can form aggregates of 0·05–0·2 μ. The cuticle keratin resembles the cement in the fibrils and has a higher cystine content than the filaments. S.B.D.

Quantitative X-Ray Study of the α–β Transformation in Keratin
V. D. Gupta
Nature, **181**, 113 (11 Jan. 1958)

If the intensities of the meridional and equatorial spots in the X-ray diagram are represented by I_m and I_e respectively, the degree of order may be defined by—

$$\text{Degree of order} = \frac{I_e - I_m}{I_e + I_m} \times 100$$

X-Ray photographs were obtained for parallel bundles of human hair held taut and capable of extension. The fibres were stretched in water at room temperature, and supercontracted by stretching in steam and allowing to recover in steam. Intensity measurements showed that there is an initial rapid rise in the degree of order, but from 60 to 70% extension the change is not large. On treatment with cuprammonium hydroxide the fibre pattern disappears because of contraction arising from an extra folding of the chains induced by coordination of copper with groups in the keratin chain. W.R.M.

Reactivity of Disulphide Bonds of Stretched Wool Fibres
J. P. E. Human and H. Lindley
Text. Research J., **27**, 917 (Nov. 1957)

An experiment resulting in stretched wool fibres losing more cystine than unstretched wool fibres when placed in a reducing soln. is described and commented upon. S.B.D.

Supercontraction of Wool in Solutions of Lithium Salts
J. Griffith and A. E. Alexander
Text. Research J., **27**, 755–767 (Oct. 1957)

The supercontraction of various types of wool, modified wool, and other keratins has been studied using concentrated solutions of lithium salts, especially the bromide. The purity of the LiBr has been found to be of considerable importance, traces of bromine in the solution having a profound effect. With Br_2 concn. in the range 10^{-4}–10^{-5}M., marked differences between clean and detergent-treated wools have been observed. Removal of the Br_2 by means of thiosulphate has enabled quantitative measurements to be made of the variables, such as concn. of LiBr, time, temperature of treatment, etc. S.B.D.

Measurement of Damage in Wool Materials. IV— A Modification of the Krais-Markert-Viertel (K.M.V.) Test— The Supercontraction of Keratin Fibres in Solutions of Caustic Potash
J. W. Bell, D. P. Veldsman, and C. S. Whewell
J.S.D.C., **74**, 85–88 (Feb. 1958)

Dimensional changes of wool fibres when immersed in 20% caustic potash solution are studied and data are given showing the effects of various chemical pretreatments on the supercontraction and the time of recovery from supercontraction. AUTHORS

Application of Statistical Theory of Elastomers to Supercontracted Keratin Fibres
A. R. Haly and M. Feughelman
Text. Research J., **27**, 919–924 (Dec. 1957)

Supercontraction of wool, human hair, and kid mohair in LiBr soln. takes place in two distinct stages. Evidence is presented which suggests that the polypeptide chains in these fibres, after supercontraction in LiBr soln., reach a condition both at the end of the first contraction stage and at the end of the second stage when the chain segments between positions of cross-linking approximate to a random configuration. The mean number of amino-acid residues in the chains between positions of cross-linking was calculated from the degree of contraction data, assuming that the chains were randomly kinked. In addition, the number was calculated from stress–strain data, using a formula which has been derived for rubber. The values obtained in these two ways were in satisfactory agreement. The nature and the distribution of cross-linkages are briefly considered, and it is pointed out that the results are consistent with cystine analyses of the fibres. S.B.D.

Molecular Organisation in Keratins. III— Densities of Physically and Chemically Modified Wools
R. D. B. Fraser and T. P. MacRae
Text. Research J., **27**, 867–872 (Nov. 1957)

A series of density determinations on physically and chemically modified wools shows that extensions of up to 70% and supercontraction of 15% in steam are not accompanied by density changes. In contrast, residues from chemical extractions and enzymatic digestions show significant increases. Cortical cells fractionated from trypsin digests by gradient-column techniques have densities comparable with that of porcupine quill tips. The extent to which these measurements may be correlated with crystallinity is discussed. S.B.D.

Elastic Properties of Chemically Modified Wools and their Implications for Theories of Wool Structure
H. Lindley
Text. Research J., **27**, 690–695 (Sept. 1957)

The changes in elastic properties produced by systematic changes in the number and kind of sulphur bonds are interpreted as implying the existence in the wool fibre of units joined longitudinally by disulphide bonds. Some possible implications of this concept are discussed. S.B.D.

Synthetic Fibres
P.-A. Koch
Z. ges. Textilind., **60**, 17–18 (5 Jan. 1958)

Tables of data. C.J.W.H.

Swelling of Cut Ends of Fibres
K. Schwertassek
Faserforsch. und Textiltech., **8**, 448–457 (Nov. 1957)

An attempt is made to systematise swelling phenomena at the cut ends of fibres. The swelling of synthetic thermoplastic fibres is influenced by heating the cut ends. Swollen fan-like or cup-like forms predominate in highly crystalline fibres, plain forms in amorphous fibres or those of low crystallinity, and conical forms in polyvinyl chloride and its copolymerisates. W.R.M.

Origin and Properties of Fibre Skin in 6-Nylon
K. Schwertassek and L. Plisek
Textil Praxis, **12**, 874–876 (Sept. 1957)

The fibre skin of 6-nylon forms as a result of faster cooling and hardening of the filament outer layers. Although the skin is more highly drawn and is in a state of higher orientation and crystallinity than the interior of the filament, its dyeing properties are the same. By

treating 6-nylon with a range of concentrations of sulphuric acid, it was possible, on a micro scale, to separate the skin from the rest of the filament. L.A.T.

Mechanical Properties of Nylon. I— Stress Relaxation in 6-Nylon at Different Humidities and Temperatures
I. Matsumoto and K. Ishikawa
J. Soc. Textile Cellulose Ind. Japan, **13**, 601–606 (Sept. 1957)

The stress-relaxation behaviour of 6-nylon stretched at various degrees of elongation was measured at 8%, 33%, 55%, and 75% R.H. and in water at 25°c.; and at 25°, 40°, and 55°c. at 55% R.H. and in water. The values of E (stress/strain) obtained at various degrees of elongation, temperatures, and R.H. were plotted against log t (sec.). The relaxation curve for nylon under various conditions could be represented approximately by—

$$\log t - \log t_0 = 1{\cdot}4 \left\{ \frac{1}{E - E_0} - (E - E_0) \right\}$$

where t is time, and E_0, t_0 are constants. The results obtained are as follows— (1) At small elongations (2%), the stress-relaxation behaviour of nylon is greatly affected by R.H. and temp. (2) At low R.H. high rates of stress relaxation are obtained at 2% and 4% elongation. (3) At high R.H. (including the tests in water) and at the greater elongations there is a small difference among the rates of stress relaxation. C.J.W.H.

Change in Properties of Polycaprolactam (6-Nylon) Fibres on Heating
G. Bodor
Faserforsch. und Textiltech., **8**, 521–523 (Dec. 1957)

The X-ray diagram of unstretched 6-nylon fibres becomes progressively weaker on heating, and at 140–150°c. the hexagonal structure changes to monoclinic. Extension does not generally alter with the crystallisation of the fibre on warming, but the elastic component decreases above 150°c. The refractive index of the fibre increases with increasing temperature. The dye absorption of stretched 6-nylon fibres decreases to a limiting value on heating to 190°c., and the time of half dyeing increases with increasing temperature of heat-treatment. W.R.M.

Polyester Fibres— Table of Properties
P.-A. Koch
Teintex, **23**, 25–39 (Jan. 1958)

Inertness, Covering Power, and Thermal Pliability of Dynel
J. M. Swalm
Text. Research J., **27**, 738–744 (Sept. 1957)

Polymerisation of Acrylonitrile and Formation of Fibres. II— Technology of the Polyacrylonitrile Fibre Nitron (Nitrolon)
E. S. Roskin
J. Appl. Chem. U.S.S.R., **30**, 1030–1041 (July 1957)

A polyacrylonitrile fibre was produced employing the principles of static polymerisation. The reaction was initiated by an oxidation–reduction medium, the agents used being $K_2S_2O_8$, $Na_2S_2O_4$, and H_2SO_4. A 98% yield of a product of mol.wt. 35,000 was obtained, when the initial temp. was 20 ± 1°c., the induction period 0–1 min., and the time of polymerisation 70–80 min. Stirring inhibited the reaction, and when its speed exceeded 120–140 r.p.m. no reaction took place. The yield was directly proportional to the initial rise in temp., and the induction period inversely proportional to the initial temp. The mol.wt. of the polymer can be controlled by means of H_2SO_4 and $Na_2S_2O_4$. T.Z.W.

Orlon Acrylic Fibre
W. W. Heckert
Text. Research J., **27**, 719–725 (Sept. 1957)

Creslan Acrylic Fibre
C. W. Bendigo
Text. Research J., **27**, 701–702 (Sept. 1957)

Acrilan— Properties and Uses
W. H. Hindle
Text. Research J., **27**, 726–730 (Sept. 1957)

PATENT

Imparting Improved Dyeing Properties to Polymeric αβ-Unsaturated Nitriles
FH *BP* 789,664

Copolymers of an αβ-unsaturated nitrile and an ethylenically unsaturated component containing a reactive ester group having an alkylating function, e.g. acrylonitrile and β-chloroethylvinylether, are given improved dyeing properties, especially as regards acid dyes, by treating them with thiourea. The treatment can be applied before the polymer is extruded into filaments or at a later stage, e.g. in the dyebath. C.O.C.

Verel Modified Acrylic Fibre (VIII p. 322)
Zefran "Nitrile-alloy" Fibre (VIII p. 322)
Darlan (Darvan) Dinitrile Fibre (VIII p. 322)
Acetalisation of Polyvinyl Alcohol Fibres with Hydroxy-aromatic Aldehydes and its Chemical Dyeing based on Coupling with Diazonium Compounds (VIII p. 322)
Acetalisation of Polyvinyl Alcohol (X p. 325)
Maturity of Cotton Fibre for Cotton Spinning. II— Differential Dyeing Method (XIV p. 328)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Mode of Action of Carboxymethylcellulose in Washing
H. Stüpel
Textil Praxis, **12**, 1009–1011 (Oct. 1957)

Dirt-suspending properties of carboxymethylcellulose have been investigated. Evidence is presented for its adsorption on the impurities and not on the fibre surface, as suggested by some authors. L.A.T.

Mode of Operation of Anti-redeposition Agents in Detergent Solutions
H. S. Stillo and R. S. Kolat
Text. Research J., **27**, 949–961 (Dec. 1957)

Application of colloid stability theory to soil redeposition liquors has enabled a working hypothesis to be formulated for the effect of polymer additives on the process. Ionogenic additives are presumed to act by increasing the electrical repulsive forces between soil and fabric, while non-ionogenic or weakly ionogenic additives may decrease the attractive dispersion forces or increase the non-electrical repulsive forces. The electrical repulsive force is inferred from soil redeposition tests to be at a maximum when the zeta potentials of the soil and the fabric are equal in sign and magnitude. As the difference in zeta potential between the two substrates is increased, an attractive force results, even though the sign of the zeta potential is the same for both substrates. This behaviour is attributed to an induced charge effect. S.B.D.

Use of Water Carriers in Theory and Practice
R. Hess
S.V.F. Fachorgan, **12**, 554–567 (Aug. 1957)

The theoretical action of water-carriers in dry-cleaning is considered with special reference to their retention of water from solvent and the saturation of the aqueous phase by water-soluble impurities, e.g. urea, salt, and sugar. The advantages and disadvantages of medium dosage (ca. 10 g./litre) and higher dosage (ca. 40 g./litre) are examined. S.R.C.

New Developments in Sodium Chlorite Bleaching
F. Schmidt
Tex, **16**, 1653–1660 (Dec. 1957)

The importance of good-quality stainless steel is stressed, especially V4A extra quality. The discontinuous process extended over 4–6 hr. and comprised impregnating machinery giving 60% expression of chlorite liquor at pH 3·6–4, followed by passage through a heater before batching in rolls of up to 1·5 metres diameter holding 3000–6000 metres of cloth. The batch rolls were slowly driven behind one another in a heating chamber at 70–75°c., and the cloth after a standing time of some hours went forward for washing off. Developments were in the direction of improved engineering of washing apparatus and impregnation facilities and in the use of individual enclosed wagons for each batch. These processes were,

however, all discontinuous, and in addition the operatives not protected from ClO_2 gas had to wear masks, which was recognised as a psychological disadvantage of the sodium chlorite bleaching process. Benteler are stated to have made possible a completely continuous working process using temp. around 95–102°C., instead of 70°C. Processing pH values are accordingly adjusted to 6·6–7 instead of 3·6–4. The process depends upon a special continuous batching chamber, where the cloth has a dwell of around 60 min. This chamber has a cloth capacity of 300–600 kg. or 3000–6000 metres of 1 metre width of weight 100 g./sq.metre. Whites sufficient for pastel dyeing are claimed, but for a full white one or two boxes of peroxide in the washing-off process are mentioned. The continuous process claims saving in space, water, steam, and chemicals and two operatives should control a production equal to that of 20–22 jigs. E.M.

Permanence of the White of Soierie Lyonnaise
P. Rochas

Teintex, **23**, 7–22 (Jan. 1958)

The durability of white on silk and viscose rayon has been studied. It was found that the fibres at room temperature and protected from light remain white indefinitely, but exposure to heat or light causes oxidation and hydrolysis. Unsuitable preparation of the fibres, e.g. excess acid on silk or hypochlorite on rayon, favours such decomposition. Whites obtained on rayon with sodium chlorite are more durable. S.R.C.

PATENTS

Continuous Peroxide Bleaching of Cotton
DuP *BP* 789,585

The desized and wet-out goods are passed through an aqueous bath containing H_2O_2 (1·25–2·0% by wt.), silicate of soda ($Na_2O:SiO_2$::1: to 1:4) (1·5–3·0), caustic soda (0·3–0·8), a water-soluble boron salt (equivalent to 0·25–2·0% borax), squeezed to 75–150% by wt. take-up, heated to 200–210°F., kept in a single continuous storage stage for 0·75–1·5 hr. at 180–212°F., and rinsed. The duration of the storage stage is such that the goods retain $\leqslant$ 15% of the H_2O_2 they contained before being heated. C.O.C.

Continuous Chlorite Bleaching of Carded Laps
Spinnfaser AG. *BP* 790,820

Carded laps can be bleached with hot aqueous chlorites at pH 4 if an openweave fabric made from glass fibres is used to carry the laps through the bath. C.O.C.

Inhibiting Corrosion of Stainless Steel by Chlorine Dioxide (I p. 313)

Change in Properties of Polycaprolactam (6-Nylon) Fibres on Heating (VI p. 320)

Surface of the Cotton Fibre. III— Effects of Modification of Soil Resistance (X p. 323)

VIII— DYEING

Determination of Performance of Fibre Blends in Wet Processing
R. C. Cheetham and H. D. Edwards

J.S.D.C., **74**, 77–85 (Feb. 1958)

The behaviour of fibre blends during wet processing such as scouring, milling, and dyeing has been studied with the object of developing laboratory techniques to simulate works conditions. A method is described for determining the behaviour of fibres under pack-dyeing conditions. In the case of fabrics, particular attention has been given to the effect of processing strains on dimensional stability. The temperature–extension curves for fabrics from different acrylic fibres show characteristic points of inflexion. Apparatus for measuring fabric crease recovery in hot liquors is described, and the information obtained has been used to study rope marking in winch dyeing. Milling has received attention with reference to felt-making, and an experimental method of evaluation has made use of small-scale machines for carding and milling. Using this technique, the effect of acid liquors of various kinds in felting has been measured. Fabric has also been used in the small-scale milling stocks to obtain the optimum conditions for milling a Fibrolane–wool velour cloth. AUTHORS

Possibilities and Limitations of the Application of Pigments to Textiles
W. Kass

J.S.D.C., **74**, 14–21 (Jan. 1958)

The fixation of pigments on various types of fibres by means of synthetic resins is discussed, and the advantages and disadvantages of this type of process are considered. AUTHOR

Theory of the Dyeing of Cellulosic Fibres
E. I. Valko

Text. Research J., **27**, 883–898 (Nov. 1957)

A complete theory of substantivity has still to await the elucidation of molecular attraction forces by physical chemistry, but this does not hinder the basic understanding of the dyeing phenomena. As a main achievement of the theory, mass action laws are formulated which explain and describe the equilibrium of dye absorption. The second achievement is that it gives a satisfactory description of the rate of dyeing, based on the concept that the rate-determining process is the diffusion of the dye from the surface of the fibre into its interior. The third achievement is the explanation of the transformations of the dye in the fibre. This was studied by X-ray diffraction and light-absorption measurements. The results indicate that soluble dyes and dye-formers are absorbed in monomolecular form by the fibre, but after they are insolubilised they exhibit in many cases a tendency to recrystallise. This explains the behaviour of azoic and vat dyes on aftertreatment. S.B.D.

Azoic Combinations in Continuous Dyeing and Discharge Printing
H. Keil

Textil Praxis, **12**, 912–917 (Sept.), 1134–1137 (Nov. 1957)

The use of azoic combinations in continuous dyeing and discharge printing is discussed. A wide range of colours of outstanding brightness and fastness properties can be obtained. Reference is also made to the application of Anthrasol dyes as a continuous process. L.A.T.

Azoic Dyeing of Nylon
J. Majzner and J. Mazurowski

Przemysl Wlokienniczy, (1), 20–23 (1957): *Polish Tech. Abs.*, (28), 127 and 129 (1957)

Three methods were tested— (1) the classical, consisting in naphtholation followed by development with the diazo component in a second bath; (2) the reversed, in which the Steelon yarn is first treated with the diazo component, then diazotised, and coupled with the coupling component; and finally (3) the method in which the material is treated simultaneously with coupling and diazo components. The last-named method— simple, rapid, and economical— yields the most favourable results, the fastest to light, rubbing, and wet treatments, with pleasant and vivid colours. This so called "patent" method, and the modified "patent" method, failed with Blues B, BB, and RT, all of which gave good results in the reversed method. The classical method, on the other hand, failed to produce satisfactory results. Yarn dyed by the "patent" method showed a loss of about 3% in strength, and with the reversed method a still greater loss in strength must be reckoned with. C.J.W.H.

Levelling Barry Nylon
H. Egli

Teintex, **23**, 40–45 (Jan. 1958)

Pad–steam techniques, swelling agents, mordants, and the Chemnyle process are discussed. Dye concentrations $\geqslant$ 0·005% promote covering. The novelty consists in using acid or chrome dyes and the sulphonated anionic auxiliaries Resoline NCP (S) or Lyogen P (S). The latter exhaust rapidly and appreciably on nylon and can block dyes of sufficiently low saturation. Differences in fibre affinity are equalised thereby. Blocking and dyeing may be effected in separate baths. Xylene Fast P dyes give good results, but a considerable number of others can be used. Sb tannate after dyeing improves the wet fastness. Lists of selected dyes are given. S.R.C.

Continuous Dyeing of Fabrics made from Polyamide and Polyester Fibres
A. Würz

S.V.F. Fachorgan, **12**, 462–474 (July 1957)

Two padding processes are described for the application of metal-complex dyes to fibres made from continuous-filament polyamide yarns. In the first method, the padding

liquor consists of a water-in-oil emulsion of the dye, and in the second process the dye is dissolved in an organic solvent with subsequent addition of a thickening agent. After preliminary drying, the colour is fixed by steaming, dry heat, or aftertreatment with dilute formic acid. In this way, it is possible to obtain fast dyeings without the risk of barriness due to physical variations in the yarns. The emulsion padding method was found useful also for the production of dark colours on polyester fibres.
L.A.T.

Verel Modified Acrylic Fibre
H. W. Coover, W. R. Ivey, W. C. Wooten, and R. T. Crawford

Text. Research J., **27**, 745–750 (Sept. 1957)

A survey is made of the physical and the dyeing and finishing properties of Verel (TE). It is a flame-resistant, thermoplastic polymer of excellent durability and is highly resistant to chemical or micro-organism attack. Verel can readily be dyed at 180–205°F. with disperse, neutral metal-complex, or basic dyes. Blends of Verel and other fibres can be dyed to give solid, reserved, or cross-dyed effects.
S.B.D.

Zefran "Nitrile-alloy" Fibre
G. W. Stanton

Text. Research J., **27**, 703–712 (Sept. 1957)

A survey is made of the physical and dyeing properties of Zefran (Dow), a "nitrile-alloy" fibre. The alloy structure is essentially a hydrophobic polyacrylonitrile backbone, containing discrete volumes of a hydrophilic dye-receptive copolymer. The fibre is very durable and can be permanently pleated. Zefran can be used in unions with natural or man-made fibres, which can be dyed to give solid, reserved, or cross-dyed effects. The recommended dyes for Zefran are the neutral-dyeing metal-complex, after-treated direct, azoic, sulphur, and vat (soluble, indigoid, and anthraquinonoid) dyes, but disperse, acid, acid-dyeing metal-complex, basic, and direct dyes can also be used.
S.B.D.

Darlan (Darvan)* Dinitrile Fibre
R. D. Smith

Text. Research J., **27**, 730–737 (Sept. 1957)

A review is made of the physical and dyeing properties of Darvan*, an alternating polymer containing approx. 50 mol.% vinylidene dicyanide $CH_2{:}C(CN)_2$ and 50 mol.% vinyl acetate. The fibre as at present produced is difficult to dye. Medium and deep dyeings can, however, be produced with disperse, basic, or azoic dyes using either carriers or high temperatures (250°F.).
S.B.D.

* The B. F. Goodrich Chemical Co. has recently announced that the name *Darvan* is to replace "Darlan" for this fibre.— *Editor.*

Mechanism of the Dyeing of Acrylic Fibres with Basic Dyes
O. Glenz

Melliand Textilber., **38**, 1152–1157 (Oct. 1957)

From measurements of the zeta potential it was deduced that surface adsorption forms an initial stage in the dyeing of acrylic fibres with basic dyes. As the temperature rises the dye molecules diffuse into the fibres. Study of dyeing equilibria and application of analytical methods such as potentiometric titrations, reaction with Malachite Green (C.I. Basic Green 4), and the carbinol base indicated the presence of active acidic groups which are responsible for the combination of dye with the fibre and whose number determines the saturation value.
L.A.T.

Acetalisation of Polyvinyl Alcohol Fibres with Hydroxyaromatic Aldehydes and its Chemical Dyeing based on Coupling with Diazonium Compounds
K. Tanabe and K. Matsubayashi

J. Soc. Textile Cellulose Ind. Japan, **13**, 623–628 (Sept. 1957)

Polyvinyl alcohol may be converted into coloured compounds of high mol.wt. with retention of the fibrous form by acetalising the heat-treated fibre with certain hydroxy-aromatic aldehydes and subsequently coupling with diazonium compounds. In order to obtain the coloured fibre resistant to boiling water, formalisation or benzalisation is generally necessary in addition to the acetalisation with the hydroxy-aromatic aldehyde. Though with a hydroxy-aromatic aldehyde having an electronegative group (e.g. NO_2, COOH, Br) directly attached to the aromatic ring acetalisation proceeds more readily than in the absence of such a group, colour development with a diazonium compound is better in the latter case, even if the degree of acetalisation is considerably lower. In particular, the fibre acetalised with hydroxy-naphthaldehyde or resorcylaldehyde to several tenths mole % may be developed in deeper colours. By changing the hydroxy-aromatic aldehyde and particularly the aromatic amine, reds, oranges, yellows, browns, purples, and blacks may be obtained, but not blues or greens.
C.J.W.H.

PATENTS

Dyeing in Urea
Courtaulds *BP* 789,243
Modification of *BP* 747,622 (J.S.D.C., 72,364 (1956))

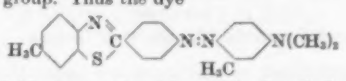
Dyeing may be carried out at > 160°C. if to the urea there is added at least one substance which is soluble in molten urea and which lowers the m.p. of the urea.
C.O.C.

Dyeing Highly Polymeric Esters
ICI *BP* 789,333

Polyester fibres are readily dyed with disperse dyes from a bath containing a chloroacetic acid, preferably trichloroacetic acid, and a wetting agent.
C.O.C.

Dyeing Polyacrylonitrile Fibres and Films
Gy *BP* 789,263

Level dyeings are obtained by use of azo dyes containing no acid water-solubilising group and at least one *cyclo*ammonium group. Thus the dye



made soluble by quaternising with dimethyl sulphate, yields a full bordeaux of excellent fastness to water and light on polyacrylonitrile when applied from an acetic acid bath.
C.O.C.

Dyeing Plastic Sheeting
Pittsburgh Plate Glass Co. *BP* 790,484

A plastic sheet is uniformly stretched longitudinally and transversely, fixed to a rigid frame, trimmed to the shape of the frame, immersed in a dye liquor, rinsed and dried. This yields very level dyeings.
C.O.C.

Dyeing and Staining of Wood
Chadeloid Corpn. *BP* 789,485

The wood is treated with an acidic or basic substance or an oxidising agent or reducing agent, e.g. sodium hypochlorite, nitric acid, sodium hydrosulphide, or stannous chloride, and then with a dye. Thus wood treated with an acidic or oxidising agent is readily penetrated by C.I. Basic Green 1 or C.I. Basic Violet 14, while that treated with a basic or reducing agent is readily dyed with C.I. Acid Orange 10 or C.I. Acid Yellow 36.
C.O.C.

Production of Naphthoylenearyliminazole and Naphthaloperinone Dyes on the Fibre (IV p. 317)

IX— PRINTING

Importance of Atmospheric Humidity in Printing
K. Lunze

Mnt. Ind., (33), 537–557 (Nov. 1957)

The decomposition of direct-style vat prints and sulphoxylated discharges is accelerated by high humidity. Particularly is this so with screen prints. In no case should R.H. exceed 45%. Control of humidity by heating, condensation, or adsorption methods is discussed. In the absence of R.H. control, replacement of K_2CO_3 by Na_2CO_3, the use of sequestering agents, and the addition of borates, HCHO, or Zn powder are suggested.
S.R.C.

Over-reduction and Over-oxidation in Printing with Vat Dyes
G. Bernardy and A. Blum

Melliand Textilber., **38**, 1159–1163 (Oct. 1957)

In printing with blue anthraquinonoid vat dyes the risk of over-reduction of the dye can be minimised by decreasing the amount of reducing agent, avoiding the use of superheated steam, keeping the steaming cycle as short as possible, and adding to the printing paste accelerators such as triethanolamine and redox buffers such as sodium nitrite, chlorite, or chlorate. Hydrogen peroxide or sodium perborate under weakly acid or alkaline conditions is suitable for prevention of over-oxidation.
L.A.T.

Mélange or Vigoureux Printing of Wool. A Method for increasing the Rate of Dye Fixation

J. Delmenico

Text. Research J., **27**, 899–912 (Nov. 1957)

The steaming time required for dye fixation has been reduced from the generally accepted 1–2 hr. at atmospheric pressure to a matter of minutes by the use of suitable solvents in the printing paste and by increased steam pressure. For example, with 5–10% benzyl alcohol in the paste, most neutral-dyeing metal-complex and many acid dyes required 10–15 min. steaming at 5–10 lb./sq.in. Chrome dyes required somewhat longer. Besides increasing the rate of fixation, suitable solvents increased the depth of colour obtained for a given amount of dye. S.B.D.

PATENTS

Applying Patterns to Cylindrical Wire Gauze Printing Screens

British Cotton & Wool Dyers' Assocn. *BP* 789,177

A metal cylinder is surrounded by and supports an extensible sleeve. The wire gauze is placed round this sleeve which is manipulated to give support to the gauze. The whole is then rotated and the screen is exposed to light under a negative carrying the desired pattern. C.O.C.

Squeegee for Screen Printing

Whitebirk Weaving Co. *BP* 789,175

Operation of the squeegee is simplified if a pair of squeegee blades are pivotally mounted on a carrier parallel to one another and one also pivotally interlinked so that they swing in parallel from one inclination to a reverse inclination, when the direction of the carrier is reversed during printing. C.O.C.

Applying Vat Dyes to Cellulose Acetate

BrC *BP* 789,547

Cellulose acetate, particularly that of acetyl value $> 59\%$, is treated with a vat dye, thiourea dioxide and zinc thiocyanate, steamed and then oxidised. C.O.C.

Oil-in-water Emulsion Textile-printing Extender Pastes

L. Auer *BP* 789,534

An extender or carrier emulsion for pigment or dyes for printing on textiles consists of a mixture of two components. The first component consists of an oil-in-water type aqueous emulsion containing a water-immiscible hydrocarbon solvent (40–66% by wt.) and a water-soluble cellulose ether (0·3–0·8%) which in 2% aqueous soln. at 20°C. has viscosity of < 120 cps. The other component is one or both of (*a*) a reinforcing oil-in-water type aqueous emulsion of a water-immiscible organic solvent solution of a water-insoluble aminoaldehyde resin, and (*b*) an elastomer latex. Such emulsions are cheap and yield prints which are fast to washing. C.O.C.

Oil-in-water Polyester Resin Emulsion Printing Colour Concentrates

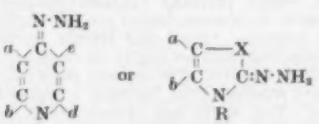
L. Auer *BP* 790,477

More concentrated pigment emulsions are obtained by first forming an aqueous dispersion of a deflocculated pigment using a fatty alcohol sulphate as the dispersing agent. A water-insoluble resinous polyester containing residues of a poly-unsaturated monocarboxylic acid is then emulsified into this dispersion in presence of a protective colloid and while preserving the pigment in its deflocculated state. This method of preparation also allows small amounts of binder to be used without impairing bonding properties to the fabric. The emulsions yield prints or dyeings of good fastness to rubbing and washing. C.O.C.

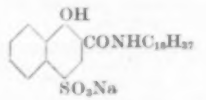
Colour Photography

Dr. C. Schleussner Fotowerke *BP* 790,327

Coloured photographic images produced by silver halide emulsions can be produced if colour couplers containing reactive methylene or methin groups are present in the emulsions and if colour developers of formula—



are used (*a* and *b* = H or together form a fused or benzene ring which may be substituted; *d* and *e* = H or Alk; R = Alk; X = S or CH:CH). An example of a suitable colour coupler is



and of a colour developer N-ethyl-2-quinolinehydrazone-hydroiodide. They yield a pure purple image. C.O.C.

Discharging Azo Dye Photographic Filters

General Aniline *USP* 2,752,244

Yellow and magenta azo dyes, e.g. those described in *USP* 2,629,658 (*J.S.D.C.*, **70**, 132 (1954)) are speedily discharged by reducing agents in presence of an *NN'*-dialkyl-4:4'-bispyridylium salt as a reduction catalyst. C.O.C.

Production of Naphthoylenearylimidazole and Naphthaloperinone Dyes on the Fibre (IV p. 317)
Azoic Combinations in Continuous Dyeing and Discharge Printing (VIII p. 321)
Applying Vat Dyes to Cellulose Acetate (IX this page)
Coated Paper-base Planographic Printing Masters (XI p. 327)

X—SIZING AND FINISHING

Physical and Thermodynamic Aspects of the Drying and Steaming of Textiles

A. Meier-Windhorst

Melliand Textilber., **38**, 1284–1288 (Nov. 1957)

Tests have been carried out to investigate temperature and moisture content changes in textile fabrics during curing, setting, drying, and steaming. Practical applications of results of these investigations are indicated. L.A.T.

History and Development of Compressive Shrinkage

F. V. Davis

J.S.D.C., **74**, 8–13 (Jan. 1958)

An account is given of the origins and development of machines for compressively shrinking cloth, and of the utilisation of such machines for special finishing effects. The main emphasis is on the Bradford Dyers' Association Ltd. machine in its various forms. AUTHOR

Surface of the Cotton Fibre. III—Effects of Modification on Soil Resistance

B. R. Porter, C. L. Peacock, V. W. Tripp, and M. L. Rollins

Text. Research J., **27**, 833–845 (Nov. 1957)

Experiments designed to complement microscopic studies and to attempt a practical evaluation of the effectiveness of various agents which impart resistance to dry soil are reported. Various natural and synthetic soils and carbon blacks (C.I. Pigment Black 6 and 7) were used, and the results interpreted from reflectance data and from radioactive tracer assays of weight of soil pick-up. It is found that grey cotton is slightly more resistant to soil than bleached cotton, and that increased smoothness of fibre, even to complete removal of native rugosities, did not necessarily impart soil resistance to cotton fabrics. The most successful types of anti-soiling agents for dry soil appear to be colloidal particulate applications such as silica or alumina, and additive finishes which lower the surface energy of the fibre. S.B.D.

Physical Properties of Fibres and Yarns of Partially Acetylated Cottons

R. S. Orr, L. C. Weiss, A. W. Burgis, and J. N. Grant

Text. Research J., **27**, 966–975 (Dec. 1957)

Samples of several varieties of cotton were partially acetylated as bulk cotton or as yarns to acetyl contents of 9–26%. Breaking loads and elongations at break of single fibres, fibre bundles, and yarns were decreased by the partial acetylation up to about 17%, but showed a tendency to increase above 20% acetyl content. Below 15%, the relation of density to acetyl content was consistent with calculations based on the preferential reaction of amorphous cellulose in the initial stages of the reaction. Resistance to heat degradation increased with acetyl content up to 25% acetyl. The pH of the water used to

rinse the reacted materials was an important factor influencing heat degradation. Maximum retention of strength occurred when the wash water was in the pH range 10–11. A slight but consistent difference in heat resistance of the partially acetylated cottons was associated with different varieties. S.B.D.

Non-aqueous Carboxymethylation of Cotton
R. M. Reinhardt, T. W. Fenner, and J. D. Reid
Text. Research J., **27**, 873–878 (Nov. 1957)

Activated cotton was impregnated with an *iso*propanol soln. of chloroacetic acid and refluxed with 0·3% NaOH in a mixture of methanol and *iso*propanol. Degrees of substitution ranging up to 0·09 were achieved. Higher values could be obtained by retreatment or by premercerisation. Four varieties of cotton were carboxymethylated by this method, and correlation has been shown between the reactivity and the original physical properties of the fibres. Textile properties of fabric treated by this non-aqueous method and those of a sample treated by the usual aqueous alkali method are compared at equal substitution. The α-methyl-, α-ethyl-, α-propyl-, α-decyl-, and α-cetylcarboxymethyl derivatives of cotton were prepared in low degrees of substitution, using the appropriate α-halogenocarboxylic acid in place of the monochloroacetic acid in the non-aqueous reaction. S.B.D.

Physical Properties of Chemically Modified Cottons. III— Effects of Mercerisation
A. W. McDonald, R. S. Orr, G. C. Humphreys, and J. N. Grant
Text. Research J., **27**, 641–648 (Aug. 1957)

Yarns from six cottons selected for their widely different inherent fibre characteristics were mercerised (1) under sufficient tension to maintain their original length, and (2) while permitted to contract freely. Fibres were removed from the yarns and were submitted to certain physical measurements. Samples of the different cottons were found to differ in their response to the treatment. Those samples with a low value of a property generally showed the greatest % change in that property. Large differences in the properties of the fibres and yarns were associated with the conditions of mercerisation, whether at constant length or slack. Mercerisation tended to equalise differences between the properties of fibres in a sample as well as between those of different samples. S.B.D.

Vapour-phase Method for Preparation of Polyacrylonitrile-coated Cotton Yarn and Physical Properties of the Product
C. H. Haydel, H. J. Janssen, J. F. Seal, H. L. E. Vix, and E. A. Gastrock
Text. Research J., **27**, 975–982 (Dec. 1957)

Acrylonitrile vapours were polymerised within and upon the individual fibre surfaces of scoured cotton yarns to yield coated products having new and interesting properties. High frictional characteristics were exhibited when one coated yarn pulled against another. Excellent resistance to rot and flat abrasion was obtained in conjunction with a slight improvement in resistance to acid degradation. No essential change in heat and weather resistance was noted. Resistance to flexing, however, was adversely affected by the presence of the polymer. These coated yarns can be prepared with essentially the same equipment and procedures as required for the vapour-phase cyanoethylation of cotton. S.B.D.

Problems of "Wash-and-wear" Finishing
F. Nestelberger
Textil-Rund., **13**, 17–26 (Jan. 1958)

The different interpretations of the term are first considered. The properties to be conferred on the fabric are next examined with respect to crease-resistance, tensile strength, rip-strength, abrasion-resistance, wash and light fastness, soil-resistance, water-absorption, air-permeability, and ironing. Differences in dry and wet recovery are stressed, and desiderata in the fibre, yarn, fabric, and pretreatment are quoted. Making-up is also included. S.R.C.

Minimum-iron Finishes on Rayon and Cotton
H. A. Wannow
S.V.F. Fachorgan, **12**, 754–766 (Dec. 1957)

The uses of Lyofix, Ureol (Ciba), and Fixapret, Kaurit (BASF) brands are exemplified on cotton. Factors influencing the results obtained are discussed, together with the special testing techniques necessary. The caustic pretreatment, resin finishing, and washing-off stages on rayon are examined in turn. S.R.C.

Crease-resist Finishing and Crease Recovery
W. Wegener
Melliand Textilber., **38**, 1096–1102 (Oct. 1957)

The effect of crease-resist finishes of varying concentration on the crease recovery and on the abrasion resistance of continuous-filament viscose rayon fabrics was investigated. The ability of the fabric to recover from creasing depends on the amount of resin and on the position of the crease in relation to the warp direction. L.A.T.

Protection of Textiles against Attack by Micro-organisms
Ciba Ltd.
S.V.F. Fachorgan, **12**, 704–711 (Nov. 1957)

Methods of rot-proofing cellulosic fabrics are discussed. Reference is made to the Arigal (Ciba) process in which the material is treated with a melamine-type resin. Tests are described designed to compare the proofing efficiency of the Arigal process in relation to other methods of protection, e.g. acetylation and cyanoethylation. L.A.T.

***iso*Cyanates in Textile Finishing**
M. Kramer
S.V.F. Fachorgan, **12**, 745–753 (Dec. 1957)

Practical applications of the poly*iso*cyanates— Desmodurs H, T_{75}, T_{65}, and T and Imprafix TH (FBy)— polyurethans, polyureas, and the bisulphite addition compound of stearyl *iso*cyanates are discussed. S.R.C.

Properties of Wool modified with Difunctional *iso*Cyanates
J. E. Moore and R. A. O'Connell
Text. Research J., **27**, 783–787 (Oct. 1957)

The reaction of wool with toluene 2:4-di*iso*cyanate and hexamethylene di*iso*cyanate is described. The treated wools exhibit greater resistance towards solubilisation in hot acid and alkali and towards attack by several other chemical agents. The wet single-fibre stress–strain properties exhibited below 30% extension are only slightly affected by treatment with *iso*cyanates. The values at break and the elongation at break, however, are considerably lowered by treatment with di*iso*cyanates, but not with phenyl *iso*cyanate. Fabric stiffness and crease recovery are only slightly affected by the *iso*cyanate pick-ups studied. S.B.D.

Flameproofing of Cellulose Textiles. I— Phosphoric Acid–Urea Process
R. Schiffner and G. Lange
Faserforsch. und Textiltech., **8**, 435–443 (Nov. 1957)

Cotton and other cellulosic fabrics are treated with (*a*) solutions of urea and phosphoric acid, and (*b*) solutions of both components containing formaldehyde. Changes in strength, flame resistance, and percentages of nitrogen and phosphorus after rinsing operations are determined and discussed. W.R.M.

Fire-resistant Treatment of Cotton with Phosphorylamide
M. L. Neilson
Text. Research J., **27**, 603–610 (Aug. 1957)

Phosphorylamide, a water-soluble phosphorus–nitrogen compound, was cured on cotton cloth to impart wash-fast fire resistance. Some loss in strength, particularly tear strength, resulted, part of which could be alleviated by use of a softener. Apparently a considerable part of the nitrogen is present in the imido (= NH) form. S.B.D.

Water Repellency
N. K. Adam
Endeavour, **17**, 37–41 (Jan. 1958)

At contact angles $> 100°$ water breaks up into droplets. The largest recorded contact angle on a smooth surface is 110° (hexatriacontane crystals). This level would give good water repellency if the liquid did not soak into the surface with time, which partially explains the hysteresis of contact angles. In Nature, higher contact angles are given by broken surfaces. Cassie and Baxter worked out the theory of apparent contact angles on regularly spaced air gaps, e.g. duck feathers. The aquatic plant *Salvinia* has a surface more repellent than feathers, composed of looped projections. The water-bug *Aphelocheirus aestivalis* is covered with hydrophobic hairs nearly perpendicular and

bent horizontally at the tips. The implications for textiles are shortly discussed. S.R.C.

Hydrogen-bonding Mechanism for the Permanent Setting of Wool Fibres
A. J. Farnworth
Text. Research J., **27**, 632–640 (Aug. 1957)

It is shown that wool fibres in which the cystine linkages have been permanently broken can be given a set in boiling water equal to that of normal fibres. Set imparted by water or steam can be released by further treatment at 10–20°c. above that used in setting. Boiling soln. of reducing agents begin to impart a permanent set in < 15 sec., and a very high degree of permanent set is obtained within 30 sec. A high degree of permanent set can be obtained in a short time at low temp. by treatment of extended fibres with a soln. of urea containing a reducing agent. The resulting set is greater than that obtainable with boiling water after prolonged treatment, or with boiling alkaline soln. The results are readily explained by breakdown and reformation of hydrogen bonds following scission of some cystine linkages. S.B.D.

Appraisal of Shrink-resistant Treatments for Wool
A. M. Sookne
Text. Research J., **27**, 652–661 (Aug. 1957)

A review is presented of the mechanisms by which wool shrinks, and of the several classes of treatment available for making shrink-resistant wool. Some of the virtues and deficiencies of the better-known classes of shrink-resistant processes are listed. The competitive position of shrink-resistant wool is examined in a number of end-use items. It is concluded that a number of low-cost, adequate shrink-resistant processes are currently available and that wool requires shrink-resistance to enable it to compete with man-made fibres in end-uses requiring ease of care. S.B.D.

Shrinkproofing Treatments— III
F. C. Mauri
Ingen. Text., **24**, 413–421 (Sept.–Oct. 1957)

Chlorination treatments discussed include gaseous (W.I.R.A., B.D.A., T.B.L.), solvent (Dri-sol), and acid hypochlorite (Kelpie, Kroy, Negafel, Hypak). S.R.C.

Chemical Damage in Wool. III— Effects of Aqueous Chlorine
W. H. Houff, C. J. Wills, and R. H. Beaumont
Text. Research J., **27**, 961–965 (Dec. 1957)

A study of the wet properties of wool exposed to low concn. of aqueous chlorine under a variety of conditions is reported. Fibre stress–strain data are presented showing the effects of variations in the concn. of chlorine, pH, temp., time of exposure, and agitation. Comparisons of cystine–cysteic acid percentages as interpreted from paper chromatograms are presented. Alkali solubilities of chlorine-damaged samples were determined, and their relation to other properties is noted. S.B.D.

Improved Methods of Chemical Shrinking
R. Steidl
S.V.F. Fachorgan, **12**, 698–703 (Nov. 1957)

Heavy-duty fabrics were treated, on a semi-bulk scale, with different resins and varying amounts of other additives. Comparative tests carried out on the finished fabrics have shown that those incorporating starch displayed best dimensional stability, tear strength, and abrasion resistance. L.A.T.

Finishing of Ladies' Hose
C. Heinrich
S.V.F. Fachorgan, **12**, 650–658 (Oct. 1957)

A brief review of practices. S.R.C.

Effect of Swelling Agents, especially Phenol, on Polyamide Fibres
H. Rath and H. Groschopp
Textil Praxis, **12**, 1026–1031 (Oct. 1957)

The possibilities of setting polyamide fibres at room temperature with aqueous solutions of phenol and other swelling agents have been investigated. Chemically set fabrics have a harsher handle than those treated with saturated steam under pressure. L.A.T.

Acetalisation of Polyvinyl Alcohol
N. Nakamura

IV— Acetalisation of Polyvinyl Alcohol with Azelaic Acid Aldehyde
J. Soc. Textile Cellulose Ind. Japan, **13**, 518–522 (Aug. 1957)

Polyvinyl alcohol can be easily acetalised with azelaic acid aldehyde CHO·$[CH_2]_7$·COOH, both in homogeneous (aqueous solution) and heterogeneous (fibrous) reactions, and the degree of acetalisation may be determined by titration of the carboxyl groups. It was difficult to obtain fibres which were sufficiently resistant to boiling water. Viscosity measurement of aqueous solutions showed that this acetal is a typical polymeric electrolyte.

V— Acetalisation of Polyvinyl Alcohol with Nonyl Aldehyde
Ibid., 580–582 (Sept. 1957)

The acetalisation of polyvinyl alcohol with nonyl aldehyde has been undertaken. Polyvinyl alcohol can be readily acetalised with nonyl aldehyde to a maximum 86·5 mol.%, in the homogeneous phase in benzene solution. The highly acetalised alcohol is soluble in CCl_4 and trichloroethylene, with a softening temperature of 30–40°c. C.J.W.H.

PATENTS

Loom-finished Cloth
FBy *BP* 788,945

Fabric woven from warps treated with an aqueous solution containing a water-soluble acrylamide or methacrylamide polymer, a methylol compound able to form a carbamide-type resin, and a catalyst, dried at 100°c., and baked, before or after weaving, at 100°c. has a finish which is fast to washing and has improved resistance to crimping. Thus a coloured cotton warp is treated with a mixture of polyacrylamide, farina, dimethylolurea, and lactic acid, dried at 70°c., woven into cloth, and then baked at 130°c. for 3 min. This yields a cloth of full, slightly stiff handle, which is very fast to repeated washing. C.O.C.

Resin Finishes
ICI *BP* 790,796

Compounds containing at least two CO·NR·CH_2OH groups (R = Alk, *cyclo*alkyl or hydroxyalkyl) are obtained by treating with HCHO compounds containing at least two amide or carbamic ester groups in which each N atom bears as substituent an alkyl*cyclo*alkyl or hydroxyalkyl radical. They are used for rendering mechanical finishes on textiles fast to washing and dry cleaning and for imparting dimensional stability. Thus cotton impregnated with a solution of *NN*¹-dimethyl-*NN*¹-dimethylol adipamide with NH_4Cl as catalyst, dried, glazed in a friction calender, and baked for 5 min. at 150°c. has a highly glazed finish of good durability to washing and dry cleaning. C.O.C.

Resin Finishes
British Paints *BP* 790,837

Soft handling resin finishes are obtained by use of an aqueous solution containing an intermediate condensate of an amino-aldehyde resin, an acidic catalyst, and an ester condensation product of a polyhydric alcohol and a mono- or poly-carboxylic acid or of a monohydric alcohol and a polycarboxylic acid. The solution must contain no alcoholate, phenolate, organic acid chloride, anhydride or salt of an organic acid which can react with the ester condensate.

BP 790,838

Many of the advantages of a condensate having a high aldehyde to amino compound ratio can be obtained without the attendant disadvantages if the two components are mixed in such proportions that final hardening of the initial condensate would give a hard, brittle resin, and then a further quantity of the amino compound added to the initial condensate. C.O.C.

Epoxy Resin Finish
Shell Development Co. *USP* 2,752,269

The material is impregnated with a solution of a polyepoxide containing at least two epoxy (–C(O)C–) groups per molecule, e.g. a glycidyl polyether of glycol having an epoxy equivalency of 1·1–3·0 and mol.wt. 300–900, and is then baked in presence of a catalyst, e.g. citric or phosphoric acid. This imparts good dimensional stability and

ability to recover from creasing, a relatively soft handle and little or no loss in strength. The treated materials have no tendency to retain chlorine. C.O.C.

Flame- and Glow-resistant Finishes for Cellulosic and Natural Protein Textiles
Albright & Wilson *BP* 788,785

The material is treated with an inorganic polymer formed by treating polymeric phosphohalogenonitrile so as to substitute a reactive group for one or more of its halogen atoms, e.g. by hydrolysis, amination or hydrazination. These reactive groups are then reacted either directly with any remaining halogen atoms of another of the polymer molecules or with the reactive group of another of the polymer molecules or with a cross-linking agent forming a bridge between polymer chains. Thus a sample of phosphochloronitrile of various degrees of polymerisation is heated in an autoclave for 8 hr. with excess liquid ammonia to yield a pale yellow solid readily soluble in water. Cotton cloth impregnated with a 50% aqueous solution of this product, dried at 105°c., baked for 15 min. at 140°c., and finally treated for 30 min. at 60°c. in 0·25% soap solution increased 9·4% in weight. It was very satisfactorily rendered resistant to flame and after-glow. C.O.C.

Self-sterilising Surfaces
W. H. Engel *BP* 788,943

Textiles, paper and other surfaces coated with a composition containing *inter alia* an alkyl thiuram sulphide and a silicone are self-sterilising. Thus a mixture of tetramethylthiuram disulphide and mono sodium mono siliconate is added to paper pulp to produce paper having a long enduring self-sterilising surface or to an aqueous resin emulsion paint for use on hospital walls. C.O.C.

Antibacterial Cellulosic Material
American Cyanamid Co. *BP* 788,968

Cellulosic material, dyed or undyed, is treated with an aqueous solution of neomycin for 5–20 min. until all the neomycin has been taken up by the fibres. It is then rinsed twice or thrice and dried at 275°F. The material retains its antibiotic activity throughout subsequent manufacturing and finishing processes even at high temperatures and also during subsequent use and laundering. C.O.C.

Rotproof Finish
BASF *BP* 789,998

The materials are impregnated with aqueous dispersions of polymers derived from acrylate or methacrylates, from vinyl esters, vinyl chloride, vinyl carbazole, vinyl lactam, styrenes, acrylonitrile and vinylidene chloride containing as the dispersing and rotproofing agent a quaternary ammonium compound derived from a tertiary amine of a *N*-heterocyclic compound containing at least five members in the ring, one of which is Alk of > 7 C, e.g. the products obtained by treating *N*-octadecylhexamethylene imine with dimethyl sulphate or benzyl chloride. Such compounds are highly substantive to the fibres. C.O.C.

Compressive Shrinking
R. R. Walton *BP* 789,261

In the continuous compressive shrinkage of fabric buckling or pleating is prevented if the length of fabric which is free to take up the compressive strains and so shrunk is made as small as possible. C.O.C.

Hair-setting Compositions
Northwestern Research Corpn. *USP* 2,750,947

Hair is readily curled or straightened by treating it with an organic lubricant and a polysiloxane which can be set in contact with the surface of the hair. C.O.C.

Fixing Creases and Pleats in Cloths containing Wool
Bombrini Parodi-Delfino *BP* 790,491

The cloth or garment is treated with a setting agent, e.g. thioglycollic acid, phenol, cresol or chloroacetic acid, rinsed free of the setting agent and then dried. At any time afterwards the desired shape, creases or pleats may be imparted by ironing or pressing at a high temperature. C.O.C.

Bacteriological Studies on Cottons (VI p. 318)
Molecular Organisation in Keratins. III— Densities of Physically and Chemically Modified Wools (VI p. 319)
Elastic Properties of Chemically Modified Wools and their Implications for Theories of Wool Structure (VI p. 319)
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Acetalisation of Polyvinyl Alcohol Fibres with Hydroxyaromatic Aldehydes and its Chemical Dyeing based on Coupling with Diazonium Compounds (VIII p. 322)
Design of a Lustremeter for Quality Control (XIV p. 328)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Fibre Crystallinity during Acid Hydrolysis
E. H. Daruwalla and P. Subramaniam
Text. Research J., **27**, 827–829 (Oct. 1957)

The change in fibre crystallinity during acid hydrolysis has been studied for various cellulosic fibres. Positive crystallisation does take place with progressive removal of the disordered regions in the initial stages of acid action. This increase in fibre crystallinity ceases at the stage at which the levelling of D.P. takes place. The changes in crystal structure have been shown to be more pronounced in regenerated celluloses than in mercerised celluloses. S.B.D.

Degradation of Cellulose by Alkali Cooking
O. Franzon and O. Samuelson
Svensk Papperstidning, **60**, 872–877 (15 Dec. 1957)

A modification of earlier experiments with native (I) and mercerised (II) cotton at 170°c. to correlate carboxyl content and D.P. Small amounts of oxygen in the cooking liquor did not affect the relation. 0·66 Carboxyl per chain molecule and negligible amounts of carbonyl groups were found in degraded cotton. Rate of degradation was greater for mercerised than for native cotton. Number of glucose residues going into solution for each break in the chain is practically independent of D.P. Data support the earlier view that the primary reaction is breaking of chain, followed by "peeling off" at one of the end-groups. Everything indicates that carboxyl groups are formed at the "peeling-off" end and hydroxyl groups at the other end, where reaction sets in. R.A.

Alkali Solubility Curve of Pulp. I and II— Fine Structure of Cellulose
O. Nakao, Y. Kurosawa, and N. Migita
J. Soc. Textile Cellulose Ind. Japan, **13**, 591–596 (Sept. 1957)

I— Hydrolysed residues (crystalline region and crystalline region containing mesomorphous region) were prepared from linter pulp, rayon wood pulp, and bleached sulphite paper pulp, by dilute acid hydrolysis for 30 min. and 3 hr. respectively, and their alkali solubilities were determined. Degraded cellulose samples were prepared from linter pulp and rayon pulp by ultraviolet irradiation, and their alkali solubilities were also determined. The influences of fine structure and D.P. on the alkali solubility curve of pulp are discussed on the basis of the results obtained.

O. Nakao, S. Miyao, and N. Migita
Ibid., 596–600

II— Linter pulp and rayon wood pulp were nitrated with two types of acid mixture and then denitrated so that the D.P. of the cellulose fell little, and the alkali solubilities and distributions of lateral order were determined on the samples thus obtained. The significance of the results obtained for the influence of fine structure on the alkali solubility curve of pulp is discussed. C.J.W.H.

Relation between Sulphate and Nitrogen Contents of Cellulose Nitrate
P. E. Gagnon, K. F. Keirstead, and B. T. Newbold
Canadian J. Chem., **36**, 212–214 (Jan. 1958)

Sulphate and nitrogen contents of cellulose nitrates prepared from mixed acids containing different amounts of sulphuric acid are compared. Sulphate content tends to decrease with increasing nitrogen content. Similar results are obtained using the same amount of sulphuric acid in mixed acids. W.R.M.

Chemistry of Unstabilised Cellulose Nitrate
P. E. Gagnon, K. F. Keirstead, and B. T. Newbold
Canadian J. Chem., **36**, 215–219 (Jan. 1958)

Cotton linters and wood cellulose were nitrated in parallel experiments with a series of mixed acids. A higher nitrogen content was obtained with the cotton, and the sulphate content of the nitrated cotton increased with

increasing concentration of sulphuric acid in the nitration mixture, while that of the nitrated wood cellulose passed through a maximum value which depended on the degree of nitration. Sulphate contents of the cotton cellulose were higher than those of the wood cellulose when nitrations were carried out under similar conditions. W.R.M.

Cellulose Phosphates as Ion Exchangers
G. Diamantopoulos
Chim. et Ind., **78**, (3 bis), 102 (Sept. 1957)

The properties of various cellulose phosphate ion exchangers have been studied with the object of finding the best conditions of preparation to obtain a product of high capacity. The esterification reaction gives products of differing value according to the conditions of temperature, composition of the phosphorylating mixture, and duration of the reaction. The stability of the ion exchangers thus obtained to repeated regeneration and their behaviour towards various cations have been specially studied. C.J.W.H.

PATENTS

Sterilising Papermaking Pulps
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An organic mercury compound is added to the pulp together with a sequestering agent, e.g. tetrasodium ethylenediaminetetra-acetate, which prevents precipitation of HgS. C.O.C.

Cast-coated Paper
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To overcome formation of release wrinkles and curling caused by the paper drying more quickly at the edges than nearer the middle of the web, the coated paper is firmly held in contact with the finishing surface, thus preventing release or slippage of any portion of the web until a preselected point of release which is determined by the line of contact of a pressure roller with the surface. At this line, 180° or more from the initial contact line, the web is separated from the drum in a straight line. R.A.

Coated Paper-base Planographic Printing Masters
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The super-calendered layer or coating consists of a dry residue of an aq. composition containing a mineral filler (such as clay), a partially etherified starch, and an amino-aldehyde resin. A hydroxyalkyl ether of starch is reacted with the amino-aldehyde resin in an aq. medium at elevated temp. The reaction is stopped; the partially reacted mixture, together with the filler, is applied to the surface base and the coated paper dried and calendered. Drying is effected at 50–150°c., but still lower curing times may be achieved on addition of an acid catalyst, e.g. monochloracetic acid. R.A.

Auto-copy Paper
Oxford Paper Co. *BP* 788,087

Coating fluids are prepared from a finely divided pigment, e.g. Satin White (C.I. Pigment White 25), a water-soluble fatty cpd., e.g. soap and/or sulphonated oils, and water. The transparent coating becomes opaque on drying, assuming the colour of the pigment, but becomes transparent again under writing pressure, revealing the contrasting-coloured base material. The coating does not become transparent under heat up to charring temp. Hardeners such as α-protein, casein, or acrylate resin, and plasticisers such as glycerine may be added. R.A.

Effect of Cellulase on the Degree of Polymerisation of Cellulose and Hydrocellulose (VI p. 318)

Distribution of Substituents in Partly Methylated Celluloses. I—Homogeneous and Heterogeneous Reaction with Methyl Sulphate (XIV p. 328)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

PATENTS

Unhairing and/or Baking Animal Skins
Société des Laboratoires Labaz *BP* 790,237

The skins are treated with active cultures of varieties of streptomyces or filtrates thereof, the varieties having been chosen because they possess caseinolytic and keratinolytic and/or an unhairing activity. C.O.C.

Tanning, Retanning, and Filling
Boehme Fettchemie *BP* 790,933

The skins are treated with a water-soluble cationic resin and then in the same or separate bath with water-soluble salts of polymeric inorganic or organic acids; if desired the treatment may be in the reverse order. The tanning obtained cannot be destroyed by acid or alkaline reagents. C.O.C.

XIII—RUBBER; RESINS; PLASTICS

Dye-sensitised Photopolymerisation of Acrylonitrile-Vinyl Acetate Copolymers
M. Taniyama and G. Oster
Bull. Chem. Soc. Japan, **30**, 856–859 (Nov. 1957)

PATENTS

Microporous Films
R. Smith-Johanssen *BP* 789,882

A finely divided thermoplastic powder of controlled particle structure is dispersed in a high viscous, inert and incompatible matrix. The dispersion is then heated so as to fuse the thermoplastic particles and then the inert material is leached out. C.O.C.

Internally Patterned Translucent or Transparent Synthetic Resins
Röhm & Haas *BP* 789,417

A foil of synthetic resin is immersed in a liquid monomer which can be polymerised to yield a translucent or transparent resin. The foil is allowed to swell in the monomer which is then polymerised in such a manner that the foil becomes distorted. C.O.C.

XIV—ANALYSIS; TESTING; APPARATUS

Fluorometric Determination of Thallium with Rhodamine B (C.I. Basic Violet 10)
H. Onishi
Bull. Chem. Soc. Japan, **30**, 827–828 (Nov. 1957)

Electron-microscopic Examination of Detergents
M. Kehren and M. Rösch
Melliand Textilber., **38**, 1295–1300 (Nov. 1957)

A freeze-drying technique is described for the examination of detergent solutions with the aid of an electron microscope. From the examination of photomicrographs it is suggested that solutions of non-ionic substances have a discrete granular structure. Anionic washing agents, on the other hand, display a lattice arrangement. L.A.T.

Evaluation of the Properties of Surface-active Agents
H. Jędraszczyk
Prace Inst. Włók. (1), WPLiS, pp. 20 (1957): *Polish Tech. Abs.*, (28), 131 (1957)

This paper describes a method, convenient for use in industrial practice, for determining the wetting qualities, resistance to sulphuric, formic, and acetic acids, resistance to hard water, ability to disperse lime soaps, and detergent properties of surface-active agents. The effect on wetting properties of concentration is determined in relation to particular agents. The most important Polish surface-active substances are examined, together with certain foreign ones. C.J.W.H.

Determination of Dye Solubility
M. Capponi
Textil-Rund., **13**, 15–17 (Jan. 1958)

A range of solutions of increasing concentration is filtered through a specifically constructed dynel fabric for which the colorant has no affinity. Any residues on the fabric are then dissolved in water and estimated in a Duboscq colorimeter (colour illustration). S.R.C.

New Colour Reactions of Phthaleincomplexone
R. Belcher, M. A. Leonard, and T. S. West
Chem. and Ind., 128–129 (1 Feb. 1958)

Phthaleincomplexone gives intense red–purple complexes with Mn, Cd, Hg^{II}, and Ag ions in an aq. NH_3 or aq. NH_4Cl–NH_3 buffer. Pb gives rise to a colour reaction in aq. NaOH similar to that observed for Zn (cf. Schwarzenbach *et al.*, *Helv. Chim. Acta*, **37**, 113 (1953)), but unsuitable for indicator purposes. In relatively conc. soln., V^{IV}, V^{V}, Co, and Ga produce less well defined pink–purple colours, but Tl^{I} forms a deep purple cpd. When an excess of sodium ethylenediaminetetra-acetate (E.D.T.A.) is added to the various metal–indicator complexes, the blue Co complex changes colour sluggishly, a moderately good

end-point is obtained with Hg^{II}, but only poor results are afforded by Ga, Pb, Sn^{IV}, and V. Both Mn and Cd may be titrated satisfactorily with E.D.T.A., and titration procedures are now given in detail. End-points are generally improved by screening the colour changes by the addition of a dye such as Xylene Cyanole FF (C.I. Acid Blue 147). Al and Fe (up to 4%) do not interfere with the end-point for Cd, in contrast to Mn, Cu, Ni, Ce^{III}, Ti^{II}, and Sn^{II}, which adversely affect it. H.H.H.

N.P.I.R.I. Standard Test Methods for Pigment Identification
C. E. Moore

Paint Manuf., **27**, 377–380 (1957): *Chem. Abs.*, **52**, 747 (10 Jan. 1958)

An outline of the tested procedures for identifying a variety of pigments including: chromates, Benzidine Yellow, Hansa Yellow, Phloxine and Rhodamine Toners, Alkali Blue, and tungstated or molybdated toners, Iron Blue, Phthalocyanine Blue and Ultramarine, sulphide pigments, Cadmium Red, and TiO_2. Notes on further tests which seem to be needed are given. C.O.C.

Fibre Replication for Light Microscopy
V. Peck

Text. Research J., **27**, 751–752 (Sept. 1957)

A method of preparing flattened aluminium replicas of fibre surfaces is described. The normal replicas are mounted on D-galactose for the fibre to be removed, and then floated on water to dissolve the sugar before remounting on clean slides. S.B.D.

Aluminium Replicas of Fibre Surfaces for Light Microscopy
A. W. Ferguson and R. G. Scott

Text. Research J., **27**, 752–753 (Sept. 1957)

A method of preparing flattened aluminium replicas of fibre surfaces is described. The normal replicas are mounted on polyacrylic acid for the fibre to be removed, and then set in polystyrene before removing the acid with hot water. After placing the replicas on clean slides, the polystyrene is dissolved away, leaving the flattened replicas. S.B.D.

Estimation of Moisture Content of Textiles by the Karl Fischer Method
A. Agster and M. Wandel

Melliand Textilber., **38**, 1411–1416 (Dec. 1957)

A procedure is described for the preparation of the Karl Fischer reagent and its application to the estimation of the moisture content of textiles. The fibrous material is extracted with anhydrous methanol and the extract is titrated with the reagent. Moisture content values of hydrophilic fibres determined by this method are slightly higher than those determined by drying the material to constant weight. Retention of water by secondary valency and capillarity forces may be responsible for this effect. L.A.T.

Maturity of Cotton Fibre for Cotton Spinning. II— Differential Dyeing Method
Y. Ono

J. Soc. Textile Cellulose Ind. Japan, **13**, 574–579 (Sept. 1957)

The growth of the cotton fibre in an upland variety was observed, and the process of maturing studied by the differential dyeing method. The relative merits of the dyeing and microscopic methods for determining percentage maturity are discussed. C.J.W.H.

Red-Green Test for Cotton
H.-P. Maier

Textil Praxis, **12**, 1075–1076 (Nov. 1957)

Theoretical aspects of the red–green test are considered. The test is used to differentiate between normal and immature cotton. The cotton is dyed with a mixture of Diphenyl Fast Red 5BL (C.I. Direct Red 81) and Chlorantine Fast Green BLL (C.I. Direct Green 26). These two dyes differ considerably in their rate of dyeing and substantivity. L.A.T.

Red-Green Test for Cotton and its Evaluation
F. W. Fleischle

Textil Praxis, **12**, 1087–1088 (Nov. 1957)

The red–green test is applied to assess the degree of ripeness (maturity) of cotton. Using the equations given in the test it is possible to express the results of the test quantitatively. L.A.T.

Quantitative Determination of *cyclo*Hexylamine in Rayon Spin Baths
M. Matell

Text. Research J., **27**, 993 (Dec. 1957)

A method of determining the *cyclo*hexylamine in rayon spin baths by distilling it into excess hydrochloric acid, and then back-titrating with NaOH, is described. A blank of the spin bath without the amine must be made to correct for any ammonium salts present. S.B.D.

Methylation of Cellulose Xanthate
B. J. Barrett and C. H. Lindsley

Text. Research J., **27**, 767–773 (Oct. 1957)

The distribution of xanthate groups along cellulose chains in commercial viscose soln. very probably affects the processing qualities and also the physical properties of the spun yarn. The xanthate groups are too unstable to permit direct determination of their location; attempts have been made to fix their position by quantitative replacement with methoxyl groups. After hydrolysis of the methylcellulose so produced to methylglucoses, various means have been used to identify the latter, but the results have not been sufficiently accurate to determine the positions of the original xanthate groups. In the present work use was made of chromatographic methods to separate and identify the products of hydrolysis. However, during a careful re-examination of the methylation procedure it has been found that about 20% of the xanthate groups were converted to the *S*-methyl ester and therefore lost during hydrolysis. Hence, although adequate means are now available for determining the positions of methyl groups in methylcellulose, better means of replacing xanthate groups must now be sought if the original problem is to be solved. S.B.D.

Design of a Lustremeter for Quality Control
T. M. Smith, H. A. Thompson, and W. I. Kaye

Amer. Dyestuff Rep., **46**, 725–730 (7 Oct. 1957)

The lustremeter consists of an incandescent light source, a collimating system without lenses, a light modulator consisting of a synchronous motor and a rotating sector (to compare reflectance by a standard magnesium oxide sample and by the yarn), a vacuum phototube, and an amplifier, detector, and meter.

Using cellulose acetate yarn, the curve of lustre against titanium dioxide content is obtained. There is a linear decrease of lustre with the number of turns of twist per inch. Lustre decreases linearly with percentage lubricant on the fibre. Winding tension does not affect lustre significantly. The statistical distribution of lustre values can be studied. P.T.S.

Distribution of Substituents in Partly Methylated Celluloses. I— Homogeneous and Heterogeneous Reaction with Methyl Sulphate
I. Croon and B. Lindberg

Svensk Papperstidning, **60**, 843–849 (30 Nov. 1957)

A method for the investigation of the distribution of substituents in methylcellulose is described. This is based on hydrolysis to glucose and glucose methyl ethers followed by a quantitative chromatographic separation on a carbon column, some components requiring further fractionation by paper chromatography and paper electrophoresis. A number of methylcelluloses prepared from cotton linters were investigated. It was found that the samples prepared by a homogeneous reaction gave quite good agreement between calculated and observed distributions. G.S.B.

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Apparatus for rapidly estimating the degree of anisotrophy in cellulose acetate film or the like. C.O.C.

Triarylmethane Compounds as Redox Indicators in the Schoenemann Reaction. III— Dyes and their Spectra (IV p. 315)
Measurement of Damage in Wool Materials. IV— A Modification of the Krais–Markert–Viertel (K.M.V.) Test— The Supercontraction of Keratin Fibres in Solutions of Caustic Potash (VI p. 319)
Molecular Organisation in Keratins. III— Densities of Physically and Chemically Modified Wools (VI p. 319)
Swelling of Cut Ends of Fibres (VI p. 319)
Determination of Performance of Fibre Blends in Wet Processing (VIII p. 321)

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The Society is urgently wanting Journals (in good condition) for October 1944, April 1954 and for all months of 1955 except July and December. The months of January, February, March, August and September 1955 are particularly required. Copies of January, February, March, April, July, August, September, October and December 1956 issues are also in demand.

Please address communications to the General Secretary

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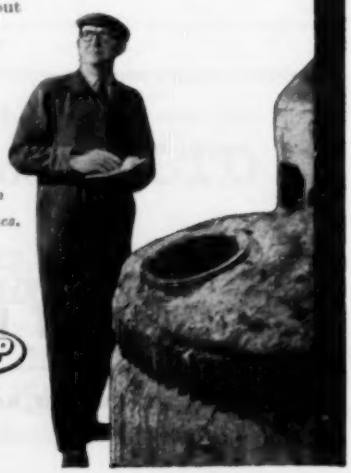

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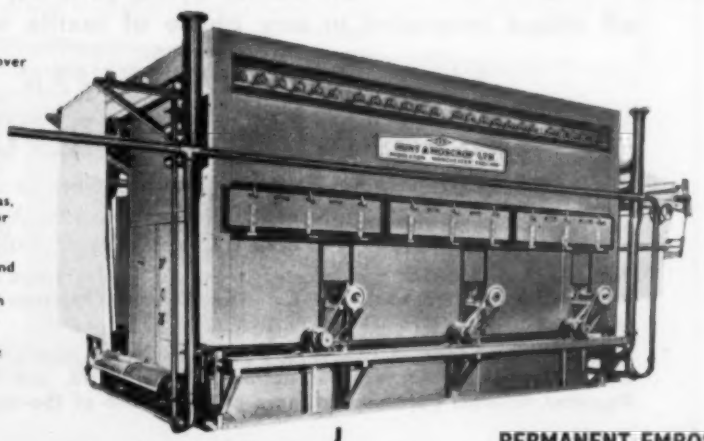

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